NEW REDUCTION METHODS IN
VOLUMETRIC ANALYSIS

NEW REDUCTION METHODS

IN

VOLUMETRIC ANALYSIS

A MONOGRAPH

BY

EDMUND KNECHT, Ph.D., M.Sc. Tech., F.I.C.

ASSOCIATE PROFESSOR OF APPLIED CHEMISTRY IN THE VICTORIA UNIVERSITY OF
MANCHESTER, AND IN THE MUNICIPAL COLLEGE OF TECHNOLOGY, MANCHESTER

AND

EVA HIBBERT, M.Sc. Tech.

ASSISTANT LECTURER IN APPLIED CHEMISTRY IN THE VICTORIA UNIVERSITY OF
MANCHESTER, AND IN THE MUNICIPAL COLLEGE OF TECHNOLOGY, MANCHESTER

SECOND EDITION

LONGMANS, GREEN AND CO.

39 PATERNOSTER ROW, LONDON, E.C.4

NEW YORK, TORONTO
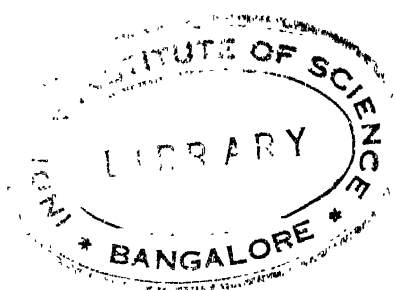
BOMBAY, CALCUTTA AND MADRAS

1925

472

545.2
N25

Made in Great Britain

PREFACE TO THE SECOND EDITION

THE whole work has been carefully revised, in part rewritten and brought up to date. While retaining the original plan of describing principles of the methods and giving proofs of their reliability in Part II, and their practical application, with selected examples, in Part III, it has been found expedient to incorporate Parts IV and V in Parts II and III. Considering the very specialised character of the subject, the demand for a new edition was unexpected, though gratifying and encouraging to the authors. The new methods have been extensively criticised, though generally in a favourable sense, and are now widely adopted for the special purposes for which they were intended. Other workers have continued to contribute to our knowledge of the subject; their results are duly recorded in the present volume.

The additional matter presented includes an "absolute" method for the estimation of glucose and other sugars, starch, cellulose, etc., which is based upon the quantitative reduction of the osazones by means of titanous chloride, a further new method for the rapid estimation of glucose, and new methods for the quantitative estimation of vanadium, diazo compounds, phenylhydrazine, hydrazones, and osazones, Michler's hydrol, isatine, tartrazine, gallein, phenolphthalein, alizarin S, oxycellulose, etc., have been added.

As in the first edition, volumetric methods have been introduced in some cases, for which alternative methods have not previously existed; in others, the new methods offer the

advantage of greater dispatch; while in others again they are recorded for the reason that they may serve in a confirmatory capacity. The chronological list at the end has been amplified and brought up to date.

<div align="right">
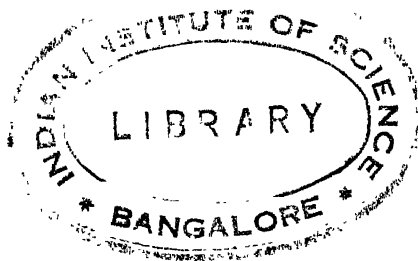
E. K.

E. H.

</div>

MANCHESTER,
  January, 1925.

TABLE OF CONTENTS

PART I

INTRODUCTION

PREPARATION OF TITANOUS SALTS. TITANOUS SALTS AS QUALITATIVE REDUCING AGENTS

PART II

TITANOUS CHLORIDE AS A QUANTITATIVE REDUCING AGENT

A. Inorganic Substances

PART III

DETAILS OF ANALYTICAL METHODS

CONTENTS

x CONTENTS

Colouring Matters in Dyed Cotton Fabrics

PAGE

Estimation of Sugars

NEW REDUCTION METHODS IN VOLUMETRIC ANALYSIS

PART I

INTRODUCTION

PREPARATION OF TITANOUS SALTS. TITANOUS SALTS AS QUALITATIVE REDUCING AGENTS

THE reducing agents at present employed in volumetric analysis include ferrous salts, stannous chloride, arsenious oxide, sodium thiosulphate, sodium hydrosulphite, and hydrazine and its derivatives.[1] Of these only thiosulphate and arsenious oxide are stable in aqueous solution when exposed to the air, and their application is almost entirely restricted to iodimetry. The ferrous salts find their principal application in the standardising of permanganate, the estimation of chromic acid and its compounds, of chlorates and of nitrates ; and stannous chloride finds some application in the estimation of ferric iron, and has been used with limited success for the estimation of nitro compounds and of some basic dyestuffs. Hydrosulphite of soda has been suggested by A. Müller [2] as a reagent for the estimation of indigo, while Rawson has used this compound successfully for the estimation of ferric iron.[3] Generally speaking, the methods of volumetric analysis based upon the use of reducing agents are relatively few as compared with acidimetric and alkalimetric, oxidation and precipitation methods. This has been largely due to the want of a sufficiently powerful (energetic) reducing agent which could be maintained at constant strength for a reasonable period. In 1847, Ebelmen,[4] in describing the

---

[1] J. Schmidt, *Die Anwendung der Hydrazine in der analytischen Chemie,* 1907.
[2] *Ber.,* 1880, p. 2283.
[3] *J. S. D. and C.,* 1885, p. 77.
[4] *Ann. Chim. Phys.,* 1847, **20**, p. 385 ; *J. pr. Chem.,* 1847, p. 70 ; *Jahresber.,* 1847–48, p. 402.

B

reactions of titanous chloride, $TiCl_3$, first drew attention to the strong reducing action of its aqueous solution, and pointed out that it was capable of reducing the salts of copper and iron to their lowest states of oxidation. A further study of the properties of this compound showed that it was well adapted to supply the want of a reducing agent of the kind mentioned, and in the following pages many cases of its successful application in volumetric analysis are recorded.

The first account of the occurrence of titanium is contained in two papers by the Rev. William Gregor, vicar of Manakan in Cornwall, which were published in 1791.[1] From the detailed description which the author gives of his experiments, it is evident that he not only recognised in the mineral then known as menakanite the presence of a new element, but that he also prepared titanous sulphate in solution, for he describes accurately some of its characteristic properties. It was not until a considerably later date that Berzelius succeeded in isolating the element. Titanium occurs not only widely distributed in nature (in rutile, titanite, ilmenite, etc., and in many clays and bauxites), but also in large quantities. In T. W. Clarke's estimate of the distribution of the elements in the solid earth's crust, oxygen and silicon account for 74·5 % of the total, while titanium is tenth with 0·33 % and carbon next with 0·22 %.

In the periodic system titanium (with the atomic weight 48) occupies the position in the fourth group intermediate between Silicon (28) and Germanium (72) ; Tin (118) belongs to the same group, but although its position in the system is considerably lower down (Zirconium intervening), it is the only element of the group of which the salts of the lower oxide (stannous salts) can be compared for practical reasons with the titanous salts.

Titanium forms four distinct oxides, viz.—

TiO, Titanium monoxide or suboxide.
Ti_2O_3 ,,   sesquioxide or titanous oxide.
TiO_2,   ,,   dioxide, titanic acid, or titanic oxide.
TiO_3,   ,,   peroxide.

The first three of these oxides yield salts with acids, those formed by TiO being blue, but little of a definite character is known of these except that they are unstable in presence of water, which they decompose with evolution of hydrogen. Those of Ti_2O_3 are generally violet and in some cases green,

[1] *Chem. Ann.*, 1791, pp. 40 and 103.

those of TiO_2 colourless (except the tannate and gallate, which are of an intense orange colour), while TiO_3 is in itself of an intense orange colour, but yields no definite salts with acids. The oxide TiO_2 is in a sense analogous to SiO_2, inasmuch as when fused with alkalies it yields titanates ; but these, unlike the silicates, are instantly decomposed by water. The alkali salts of TiO_3 (pertitanates) are colourless.

Preparation of Titanous Chloride.—The anhydrous salt is obtained by passing a mixture of the vapour of titanic chloride and hydrogen through a red-hot tube. Reduction takes place with simultaneous formation of hydrochloric acid, the titanous chloride being deposited on the cool parts of the tube in the form of scales of a dark violet colour which deliquesce in moist air, forming a reddish-violet liquid.

Böck and Moser [1] describe, in addition, a brown modification which differs besides from the violet by its heat of solution in water.

Aqueous solutions of titanous chloride may be prepared more readily and in several ways, *e.g.* by dissolving the metal in strong hydrochloric acid, in which it dissolves readily with a bright blue colour while hot, becoming violet on cooling ; by reducing a solution of titanic chloride in hydrochloric acid with different metals, such as zinc, aluminium,[2] copper, mercury,[3] etc. The most suitable of these metals is zinc, either in the form of powder or in the granulated condition. The cleanest and most convenient means of obtaining the aqueous solution is, however, by the electrolytic reduction of a solution of the tetrachloride, or by double decomposition of the electrolytically prepared titanous sulphate [4] with barium chloride. But although the preparation of the salt in the laboratory is not a matter of any difficulty, the time and trouble involved would probably deter most chemists from trying the methods detailed in the following pages. For some years past the product has been manufactured on a large scale, and is placed on the market in the form of a 20 % aqueous solution at a price which renders it available for commercial or scientific work. It should be pointed out that this product

---

[1] *Monatsh.*, 1913, p. 1825.

[2] T. J. I. Craig and Peter Spence & Sons, Engl. P. 13260, 1911.

[3] The reaction with copper seems to be a reversible one, for titanous chloride added to a solution of cupric sulphate will precipitate a portion of the copper as metal. Mercury behaves in a similar way to copper.

[4] N. Evans, *Mem. Manch. Lit. and Phil. Soc.*, 1904, vol. 49, II. p. 1. Also Diethelm and Foerster, *Z. phys. Ch.*, 1908, p. 132.

may contain small amounts of ferrous chloride, which, however, does not interfere with any of its applications detailed in the sequel, except for the estimation of chromium, hydrogen peroxide, and persulphates. More recently, however, a solution of pure titanous chloride has been placed on the market which only contains traces of iron, and is therefore specially adapted for analytical work.

By saturating the concentrated aqueous solution with hydrochloric acid gas, a crystallised salt, having the composition $TiCl_3 + 6H_2O$ is obtained, in the form of violet crystals, but experience has shown that in this form the salt is of little practical utility, on account of its being too readily oxidised in contact with the air.

Properties and Qualitative Reactions of the Titanous Salts

In dilute aqueous solution titanous chloride exhibits a beautiful amethyst colour, but on prolonged exposure to the air oxidation takes place ; the colour gradually fades, and a precipitate of titanic hydrate forms. The formation of this precipitate may be obviated by the addition of hydrochloric acid in the proportion of one volume of the strong acid to one volume of the commercial solution. Rendering the solution strongly acid does not, however, prevent oxidation by air contact. For this reason it is necessary to store the solution of titanous chloride (likewise that of the sulphate) when intended for volumetric estimations under hydrogen, which is supplied automatically from a small generator at 2–3 in. water pressure (see p. 63).

By the cautious addition of an alkali to the solution the colour becomes bluer, while excess of alkali throws down the whole of the titanium as black hydrated titanous oxide (sesquioxide). This immediately begins to decompose the water, and on slightly warming, a brisk evolution of hydrogen takes place—

$$Ti_2O_3 + H_2O = 2TiO_2 + H_2$$

the colour of the precipitate changing from black to white.[1] Exposed to the air, the black precipitate rapidly takes up oxygen and yields titanic hydrate.

[1] It is remarkable that if the titanous chloride has been formed by the action of tin and hydrochloric acid on titanic chloride, the black precipitate which is obtained by adding excess of caustic soda changes very slowly, and can even be boiled, filtered, and dissolved in hydrochloric acid if these operations are conducted rapidly.

The reducing action of titanous chloride is, in the great majority of cases, far more energetic than that of stannous chloride or of other soluble acid reducing agents. With strong nitric acid it reacts violently with evolution of nitrous fumes, a portion of the nitric acid being reduced as far as ammonia. In dilute aqueous solutions strongly acidulated with hydrochloric acid, the reduction of nitric acid takes place, on boiling, to a stage which is intermediate between nitric oxide and nitrous oxide. If, however, an acceptor is present in the form of a primary aromatic amine and the amount of titanous chloride is limited to the proportion $2TiCl_3 : HNO_3$, reduction takes place to HNO_2 with the result that quantitative diazotisation is effected in the cold.[1] On adding slowly the commercial (15 %) titanous sulphate to concentrated sulphuric acid, the latter is instantly reduced to sulphurous acid. The action ceases, however, as soon as the sulphuric acid becomes diluted by its own volume of water. Chlorates are reduced to chlorides, perchlorates in presence of sulphuric and oxalic acids are likewise reduced to chlorides. Hydrogen peroxide is reduced to water at the ordinary temperature. Salts of persulphuric acid are reduced to sulphates. With sulphurous acid the reaction offers exceptional interest, inasmuch as this acid is reduced instantaneously to hydrosulphurous acid. Thus, on adding a solution of titanous chloride acidulated with hydrochloric acid to one of sulphurous acid or one of its salts (*e.g.* bisulphite of soda), the violet colour instantly changes to a deep orange-brown, which in a few seconds becomes orange. If excess of caustic soda now be added to the solution and the latter is filtered, the hydrosulphite is found in the filtrate. This constitutes a convenient and rapid laboratory method for the preparation of hydrosulphite of soda for qualitative work. The orange solution alluded to above, which contains the free hydrosulphurous acid decomposes on standing, but more rapidly on boiling, with deposition of sulphur and evolution of sulphur dioxide.

As shown by Ebelmen, ferric salts are reduced to ferrous salts, and it was ascertained that this reduction is quantitative (see below) and takes place in the cold.

Cupric salts are first reduced to cuprous salts, but on adding excess of titanous chloride to a solution of copper sulphate, a portion of the copper is precipitated as metal. Conversely, if titanic chloride is heated with metallic copper, a partial reduction to titanous chloride takes place.

[1] *J. C. S.*, 1924, p. 1537.

In its action on mercuric chloride, titanous chloride offers a somewhat curious anomaly, for whereas the much weaker stannous chloride instantly precipitates white mercurous chloride, which by excess of the reagent is further reduced to metallic mercury *in the cold*, titanous chloride is without action under these conditions, and only reacts on boiling the solution, when reduction takes place. Conversely mercury in large excess reduces titanic chloride to titanous chloride, in the cold.

Arsenic acid is reduced by titanous chloride in hydrochloric acid solution to arsenious acid, while stannous chloride brings down metallic arsenic under these conditions. In presence of Rochelle salt (sodium-potassium tartrate) and at the boil, titanous chloride gives a copious brown-black precipitate, which apparently consists of metallic arsenic.

Salts of chromic acid are instantly reduced to chromic salts, and permanganates to manganous salts.

Stannous chloride has apparently no action on titanic chloride, while on the other hand titanous chloride does not appear to react on stannic chloride.

Molybdic, tungstic, and vanadic acids are turned blue by titanous chloride.

The reducing action of titanous chloride on organic compounds is likewise of interest. In the fatty series, oleic acid is reduced to stearic acid, and fumaric and citraconic acids to succinic and pyrotartaric acids respectively. Prussian blue is rapidly decolourised, but the colour of the resulting white compound soon returns to that of the original on exposure to the air.

With potassium ferrocyanide, titanous chloride yields an intensely orange-yellow precipitate, which becomes green on heating.

In the aromatic series a far larger proportion of compounds have been found to give definite reactions with titanous chloride. Thus, the nitro compounds are readily reduced to the corresponding amines. By limiting the amount of reducing agent, it was found possible to reduce one nitro group in m-dinitro benzene, a good yield of m-nitraniline being obtained. Nitroso-dimethylaniline is quantitatively reduced at about 40° C. to dimethyl phenylene diamine.

Of the oxyazo and amidoazo compounds all that have been tried were completely reduced with consequent permanent decolourisation, and there is no reason to suppose that the reaction is not in all cases a quantitative one. A remarkable

anomaly was found in the behaviour of Diamine sky blue and Chrysophenin towards stannous chloride and titanous chloride respectively. The first of these dyestuffs is readily reduced by excess of either reagent, whereas Chrysophenin is only reduced by titanous chloride. If now a mixture of the two dyestuffs is treated with stannous chloride, the blue is discharged, leaving the yellow, as would have been expected. But if the mixture is treated with a limited amount of titanous chloride, the yellow is discharged, leaving the blue. Similar selective reduction, though less pronounced, was also found in other mixtures of azodyes.

Nearly all the dyestuffs which are capable of yielding leuco compounds are reduced by titanous chloride. Thus, finely divided Indigo is reduced first to indigo white, but by the action of a large excess of the reducing agent and at the boil, it is reduced past the condition of indigo white, yielding a yellow substance, which is not reconverted into indigo by oxidation.

Methylene blue,[1] Safranine, and New blue are readily reduced, and are reoxidised by mere contact with the air. The dyestuffs of the triphenylmethane series and their sulphonic acids are reduced in presence of excess of Rochelle salt,[2] and the same applies to the sulphonic acids of Indigotine, Indirubine, Thioindigo red, Rosinduline, etc.

The Eosines and Rhodamines can be reduced in presence of Rochelle salt and alcohol, whereas all attempts that have hitherto been made to reduce Auramine, Primuline, and Thioflavine have failed. Aniline black is readily reduced by titanous chloride to a dull brown product. The sulphide colours are likewise reduced, but evidently some change other than mere reduction to the leuco compounds must occur, as they give off considerable quantities of sulphuretted hydrogen. This reaction may be used as a qualitative test for sulphide colours in dyed cotton yarns or fabrics.[3]

[1] The reducing action of titanous chloride on Methylene blue may serve as a very delicate test for titanium in qualitative analysis. The solution to be tested is warmed for a few minutes in a test-tube with zinc and hydrochloric acid, and is then added to a very dilute Methylene blue solution. If titanium is present decolourisation takes place. It is possible in this way to detect titanium in amounts of even less than 0·00001 grm. (*Chem. Ztg.*, 1907, p. 639).

[2] It is found preferable to use tartrate of soda in place of Rochelle salt in these titrations, since the mineral acid in solution or from the titanous chloride produces the sparingly soluble acid tartrate of potash from the latter. This often separates out in considerable amount and is liable to interfere with the titration. According to Piccard (*Ber.*, 1909, p. 4341), the tartaric acid exerts a catalytic action on the reduction. He recommends the addition of 1 % hydrofluoric acid, which acts similarly.

[3] For some unaccountable reason, commercial titanous chloride has

Hæmateïn, the colouring matter of logwood, is reduced in presence of Rochelle salt and acetine.

With colouring matters like Indoïne (diazotised Safranine combined with betanaphthol) and Methylene green (Nitromethylene blue), which contain two chromophores, titanous chloride exerts a selective action as far as the chromophores are concerned. Thus, in reducing Indoine, the azo group is first attacked, and the red colour of the Safranine appears, which on further action is decolourised. In the case of Methylene green, it would appear that the nitro group is first attacked, since by limited action the colour changes from green to the blue colour of amido-methylene blue, and this vanishes on further addition of the reagent.

Quinone is quantitatively reduced by titanous chloride to hydroquinone, anthraquinone to anthranol, and benzil to benzoïn.

Titanous sulphate, $Ti_2(SO_4)_3$, is obtained by reducing titanic sulphate by means of zinc and sulphuric acid, or by electrolysis. It is more difficult to crystallise than the chloride, but forms double salts with sodium sulphate, which crystallise easily. The salt, having the composition $Ti_2(SO_4)_3 . Na_2SO_4 . 5H_2O$, is readily salted out from its deep purple-black solution at the boil, and crystallises in cubes of a lilac colour, readily soluble in water. The double salt, $Ti_2(SO_4)_3 . Na_2SO_4 . 12H_2O$, is obtained by spontaneous evaporation of the solution in much larger crystals, which apparently do not belong to the regular system. Commercial titanous sulphate contains 20 per cent. $Ti_2(SO_4)_3$, and is duller in colour than the chloride. When diluted strongly with water it yields a somewhat turbid solution, the turbidity being caused by the presence of a little titanic sulphate, which dissociates, yielding titanic hydrate.[1]

As a reducing agent, titanous sulphate reacts in most cases like the chloride. In the case of copper sulphate, however, it precipitates the copper quantitatively as metal. The reaction is a very delicate one, and is still visible in solutions containing one part of copper in a million.[2]

occasionally been found to contain traces of sulphuretted hydrogen. If used as a test for Sulphide colours, it should therefore be boiled with the addition of some hydrochloric acid before use.

[1] The slow decomposition of titanic chloride and sulphate is apt to result in the formation of a white deposit on the containing vessels, which is difficult to remove by the ordinary reagents. Dilute hydrofluoric acid or a hot solution of potassium binoxalate are the best means for removing this deposit.

[2] *Mem. Manch. Lit. and Phil. Soc.*, 1904, No. 9.

PART II

TITANOUS CHLORIDE AS A QUANTITATIVE REDUCING AGENT

A.—*INORGANIC SUBSTANCES*

The Interaction of Titanous and Ferric Salts [1]

IN order to ascertain whether the reduction of ferric salts by titanous salts is quantitative, potassium titanic fluoride which had been recrystallised several times was chosen as standard. An accurately weighed quantity of this salt was reduced by zinc and hydrochloric acid in a flask provided with a Bunsen valve, and the cooled solution [2] titrated in a current of carbon dioxide with a solution of ferric chloride of known strength until a sample withdrawn at the end of a glass rod and spotted with potassium sulphocyanide gave a faint red colouration. [3] The following results were obtained :—

K_2TiF_6 . Calc. Ti = 18·60 % Found Ti = 18·42, 18·40, 18·56 %

The gravimetric determination gave Ti = 18·47 %.

Similar results were obtained using recrystallised titanium potassium oxalate, $TiO . C_2O_4 . K_2C_2O_4 . H_2O$ as standard. It is evident, therefore, that the reduction of ferric salts by titanous salts is quantitative, and takes place according to the scheme—

$$TiCl_3 + FeCl_3 = TiCl_4 + FeCl_2$$

and that we have in this reaction a convenient means for the

---

[1] *Ber.*, 1903, 1549.

[2] Instead of being violet, as might have been expected, the solution is green, this colour being probably due to the formation of a double salt of titanous fluoride and potassium fluoride, for titanous fluoride itself is violet.

[3] The spot test was soon afterwards abandoned, as it was found that the direct addition of potassium sulphocyanide to the contents of the flask did not in any way interfere with the delicacy of the reaction, and was much more convenient. It should be noted, however, that a considerable excess of the indicator must be used, as ferric sulphocyanide is decolourised by strong dilution.

9

estimation of ferric iron on the one hand and of titanous and titanic (after reduction) salts on the other.

Iron

The principle involved in the volumetric estimation of iron by titanous chloride is stated on p. 68. It is, of course, essential that the iron should be present in the ferric condition and that no nitric acid or other substance liable to exercise an oxidising action be present in the solution. In using potassium sulphocyanide as indicator, a large excess of this must be added to ensure a sharp and definite end point, while if Methylene blue is used, the solution should either be heated to about $35°$ or the indicator activated by the addition of one drop of a 10 % solution of salicylate of soda, in which case titration can be effected in the cold. Using either of these indicators, back-titrating with standard iron alum solution may be effected in case of need.

For the volumetric estimation of ferric iron it is claimed that the titanous chloride method, while not ceding anything in point of accuracy to the permanganate method, is considerably more convenient owing to the rapidity with which estimations can be carried out.

Titanium [1]

The solution of the titanic compound is reduced with zinc and hydrochloric acid in a conical flask provided with Bunsen valve.[2] The reduced solution should not be exposed to the air and should be titrated as soon as possible after reduction, in an atmosphere of carbon dioxide, with standard iron alum employing either potassium sulphocyanide or Methylene blue as indicator (see Iron).

Titanium may also be estimated by means of a standard solution of Methylene blue. It is first reduced by zinc and hydrochloric acid to titanous chloride, and the solution is titrated in a current of carbon dioxide with standard Methylene blue (*q.v.*) until a permanent blue colour results. Using titanium potassium fluoride as standard, the following figures were obtained :—

Experiment.	Titanium by methylene blue.	By iron.	Gravimetric.
1	18·54 %	18·56 %	18·47 %
2	18·46 ,,	—	—
3	18·38 ,,	—	—

Theoretical titanium $= 18·60$ for $K_2TiF_6 . H_2O$

[1] *Ber.*, 1903, p. 1550.   [2] *J. S. C. I.*, 1909, p. 189.

Titanium potassium oxalate (dried at 100°) analysed by the same process gave—

$$14 \cdot 76 \% \text{ Ti}$$
Calculated for $TiO . C_2O_4 . K_2C_2O_4$ . . . . $15 \cdot 07 \% \text{ Ti}$

The authors have invariably used zinc and hydrochloric acid for the reduction of the titanic to titanous salt and have experienced no difficulty in working by the methods described, reduction being complete in about 15 minutes unless much iron is present when it takes a somewhat longer time. The effect of the presence of iron in retarding the reduction of the titanic salt appears to have been noticed by several observers. Whether the salts of both metals are reduced simultaneously or whether there is selective reduction is not clear, though if the titanic salt were reduced first, the resulting titanous salt must instantly react on the ferric salt with consequent regeneration of titanic salt. If, therefore, selective reduction occurs it will be the ferric iron which is reduced first. A satisfactory explanation of the retarding action of the iron on the reduction of the titanic salt has, however, not been advanced up to now.

In carrying out the reduction with zinc and sulphuric acid, after the manner of the usual reduction of ferric to ferrous iron, Gallo [1] states that 5 hours were required for the reduction of the titanium from the titanic to the titanous condition, but that in presence of iron the time required was 12 hours. In his method, reduction with sulphuric acid is necessary in order to allow of the titration of the total titanous and ferrous salts by permanganate. The time required for reducing in sulphuric acid solution was reduced to about 15 minutes by P. W. and E. R. Shimer [2] by effecting the reduction of the hot solution in a Jones reductor filled with amalgamated zinc granules. The reductor used consisted of a glass tube of $\frac{3}{8}$-in. bore and 36 in. long. W. D. Treadwell [3] found that by employing electrolytic crystallised cadmium in place of zinc, the reduction of titanic to titanous sulphate can be effected in a much shorter time. Using a reductor tube of about $\frac{3}{4}$-in. bore containing a layer of crystallised cadmium $3-3\frac{1}{2}$ in. in depth, reduction was complete in two minutes. Morley and Wood [4] have suggested the use of aluminium foil and hydrochloric acid. As a works method,

[1] *Att. acc. Lincei.*, 1907, p. 325.
[2] *Internat. Cong. App. Chem. Rep.*, 1912, p. 445.
[3] *Helv. Chim. Act.*, 1921, p. 551, and 1922, p. 732.
[4] *J. C. S.*, 1924, p. 518.

Mr. Joseph Barnes [1] has for many years employed ordinary lead shot as reducing agent in the estimation of titanium, with satisfactory results.

Alloys have also been suggested as means for accelerating the reduction of titanic to titanous salts. Thus, Hinrichsen [2] has proposed the use of an alloy of zinc and magnesium in presence of hydrochloric acid for the purpose, while Gemmell, [3] who tested several alloys for the reduction, gives preference to one consisting of 90 % zinc and 10 % aluminium. C. van Brunt [4] has suggested a modification of a different kind in the employment of an electrically-heated reductor.

Titanium and Iron in Admixture

In a solution containing the titanium in the titanic and the iron in the ferric condition, the iron is best titrated directly with standard titanous chloride. To ascertain the amount of titanium present another portion of the solution is reduced with zinc and hydrochloric acid and titrated with standard iron alum solution.

Since Methylene blue is not reduced by ferrous chloride in hydrochloric acid solution, a titration of the reduced solution containing the two elements only gives the titanium. The iron can be estimated in the unreduced state by direct titration with titanous chloride. To prove that the estimation of the titanium is not affected by the presence of iron, mixtures of known quantities of titanium and iron were prepared, the titanium being estimated by the Methylene-blue method.

Experiment.	Titanium found.	Titanium taken.	Iron taken.
	grm.	grm.	grm.
1	0·03089	0·03094	0·01469
2	0·03867	0·03868	0·03085
3	0·00778	0·00774	0·02938
4	0·00309	0·00309	0·04876
5	0·00158	0·00158	0·04876

When much iron is present, it is necessary to allow the zinc to react for at least twenty minutes in order to ensure complete reduction.

[1] Private communication.   [2] *Chem. Zig.*, 1907, p. 189.
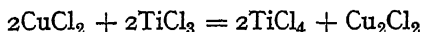[3] *The Analyst*, 1910, p. 198.   [4] *J. A. C. S.*, 1914, p. 1426.

Gallo [1] divides the reduced solution into two halves, in one of which he titrates the titanium by means of standard iron alum, while in the other he titrates the total iron and titanium by means of permanganate. The iron is ascertained by difference.

W. M. Thornton [2] has shown that titanium can be precipitated quantitatively from a mixture of titanic and ferric chlorides by means of cupferon (nitrosophenyl hydroxylamine) and weighed as $Ti(NO . NC_6H_5O)_4$. In a later paper, Thornton and Chapman [3] have compared the results obtained by this mode of separation with those obtained by the methods described in the present volume and have found them satisfactory.

Copper [4]

By acting on a cupric salt which does not contain oxidising acids (*e.g.* nitric or chloric acids) with titanous chloride, the first effect is to reduce the cupric to the cuprous salt, which separates as a white precipitate. If the titration is done in presence of a known amount of ferric salt and excess of potassium sulphocyanide, selective reduction ensues, the whole of the copper being reduced before the ferric iron is attacked. The end point is reached when the cupric and ferric salts have been reduced to the cuprous and ferrous conditions respectively, so that by subtracting the number of cubic centimetres of titanous chloride required for the known amount of iron present from the total number of cubic centimetres, the difference represents the amount of titanous chloride used for reducing the copper. The reduction may be represented by the following equation :—

$$2CuCl_2 + 2TiCl_3 = 2TiCl_4 + Cu_2Cl_2$$

Experiment having shown that cupric salts are readily reduced by ferrous salts in acid solution, and that the amount of titanous chloride used in a copper estimation was the same with or without the addition of pure ferrous salt, the mode of titration was simplified by adding ferrous sulphate and potassium sulphocyanide to the copper solution and titrating direct with titanous chloride.

An amount of copper sulphate corresponding to 0·04988 grm. of copper titrated in this way yielded 0·04986 grm. of the metal. A sample of electrolytic copper tested by the electrolytic,

[1] (*l.c.*)
[2] *Am. J. Sc.*, 1914, p. 173.
[3] *J. Am. C. S.*, 1921, p. 91.
[4] E. L. Rhead, *J. C. S.*, 1906, p. 1491.

the potassium iodide, and titanous chloride methods gave the following results :—

Method.	Copper taken.	Copper found.	Percentage.
Electrolytic . . .	0·25 grm.	0·2498 grm.	99·92
Iodimetric . . .	0·25 ,,	0·2497 ,,	99·88
Titanous chloride .	0·25 ,,	0·2496 ,,	99·84

Copper and Iron in Admixture

In mixtures of copper and iron both metals are estimated by the method described for the estimation of copper. Rhead mentions that the copper may be determined separately by removing the iron as acetate and then titrating the copper. The authors prefer to remove the copper as sulphide with sulphuretted hydrogen, and then oxidise the iron with ammonia and hydrogen peroxide, then boil off, acidify, and titrate with titanous chloride according to the method described under Iron.

In place of proceeding in this manner, W. M. Thornton (*J. Am. Chem. Soc.*, 1922, p. 998) first estimates copper and ferric iron together by titration with titanous sulphate in presence of sulphuric acid and ammonium sulphocyanide. The solution is then boiled to coagulate the cuprous sulphocyanide, and the whole of the sulphocyanide precipitated by the addition of a sufficiency of concentrated silver nitrate solution. The ferrous iron is then estimated in the cooled solution by titration with permanganate.

A. Monnier [1] has suggested another method of estimating copper and iron in admixture, employing two indicators. In one portion of the solution, copper and iron are estimated together by titrating with titanous chloride, using Safranine or Induline as indicator. By titrating a second portion of the solution with Methylene blue as indicator only the iron is estimated and the copper is arrived at by difference.

Chromium [2]

On chromic salts titanous chloride has apparently no action, but the salts of chromic acid are quantitatively reduced to chromic salts by this reagent. By adding a solution of titanous chloride to a salt of chromic acid containing ferric iron, selective action takes place, the chromic acid being reduced before the ferric iron. No advantage can, however, be taken of this when

[1] *An. de Chim. Anal.*, 1916, p. 109.
[2] S. B. Jatar, *J. S. C. I.*, 1908, p. 673 ; E. Hibbert, *ibid.*, 1909, p. 190.

potassium sulphocyanide is used as indicator, the latter being oxidised by the chromic acid, with the formation of persulpho-cyanogen. But by adding excess of titanous chloride to the chromic acid solution and then titrating back with standard iron alum in presence of sulphocyanide, the estimation of the chromium can be readily effected.

The method is also applicable to chromic salts by converting these into chromates and then titrating as described above. To prove this, a known weight of pure bichromate of potash was reduced to chromic chloride by boiling with strong hydrochloric acid. The chromium was then converted into chromic acid by boiling with sodium peroxide for about ten minutes. Ammonium chloride was then added, and the boiling continued for a few minutes. The solution was then cooled, acidulated with hydrochloric acid, and titrated as indicated above. The amount of chromium found expressed as bichromate of potash was 99·78 %.

Chromium may also be estimated, according to Atack,[1] by the following procedure :—

The chromic salt is converted into chromate by oxidising with sodium peroxide, boiling to destroy excess of the latter and running the solution into an acid solution containing excess of leucomethylene blue. The Methylene blue resulting is titrated with titanous chloride. The method was tested on pure potassium bichromate which gave 99·9 %.

For modifications of the method of estimating chromic acid, see Part III., p. 74.

A sample of pure potassium bichromate titrated by this method gave 99·90 %.

When chromates or chromic salts are reduced with zinc and hydrochloric acid, they give rise to blue chromous chloride, $CrCl_2$. It is highly probable that this salt reacts with a ferric salt in the following manner :—

$$CrCl_2 + FeCl_3 = CrCl_3 + FeCl_2$$

Attempts were made to utilise this reaction for estimating chromium, but failed in consequence of the chromous chloride immediately beginning to revert to chromic chloride with evolution of hydrogen. The results were consequently far too low. Using chemically pure bichromate of potash as standard, the reduction was effected in a cylindrical tap funnel closed at the top with an indiarubber stopper provided with a Bunsen valve. Although the reduced solution was run straight into

[1] *The Analyst*, 1913, p. 99.

excess of iron alum contained in a flask through which a current of carbon dioxide was maintained, the highest result obtained was 97 % $K_2Cr_2O_7$. The method is therefore of no practical value.

Chromium and Iron in Admixture

For this estimation, the chromium must be present as chromic acid and the iron in the ferric condition. To a portion of the solution, excess titanous chloride is added and the amount of titanous chloride used up is ascertained by back-titration with iron alum. Another portion of the solution is boiled with strong hydrochloric acid in presence of a few drops of alcohol to convert the chromic acid into chromic chloride and the iron is then titrated with titanous chloride.

Copper and Chromium in Admixture [1]

In an acidulated solution containing cupric sulphate (or chloride) and a salt of chromic acid, both constituents can be estimated by two separate titrations with titanous chloride. The first titration gives chromium and copper. Another portion of the solution is then treated with sulphurous acid, and, after boiling off the excess of the latter, is titrated again. This gives the copper only. The following results were obtained :—

	Amount taken.	Amount found.
Cr_2O_3	0·02537 grm.	0·02537 grm.
CuO	0·06360 ,,	0·06353 ,,

If, however, the chromium is present as chromic salt, it is not possible to oxidise it quantitatively to the condition of chromic acid by boiling with sodium peroxide, since the copper seems to interfere with the reaction. The mode of procedure followed in this case was first to titrate the copper with titanous chloride in an aliquot part of the solution. In another portion the copper was first removed by sulphuretted hydrogen, the chromium oxidised in the filtrate to chromic acid by boiling with sodium peroxide, with the addition of ammonium chloride, and titrated with titanous chloride. The method was tested with known amounts of copper sulphate and potassium bichromate, the latter being reduced to chromic chloride by boiling with strong hydrochloric acid. The following results were obtained :—

	Amount taken.	Amount found.
Cr_2O_3	0·02537 grm.	0·02541 grm.
CuO	0·03180 ,,	0·03185 ,,

[1] *J. S. C. I.*, 1909, p. 189.

Copper, Chromium, and Iron in Admixture [1]

In a mixture of CuO, Cr_2O_3, and Fe_2O_3, the three metals can be estimated in the following way : The mixture is fused with potassium bisulphate in a porcelain crucible, the melt taken up with water and made up to a known volume. Aliquot portions of this solution are then treated as follows :—

(1) Iron and copper are titrated together with titanous chloride.

(2) The copper is removed by means of sulphuretted hydrogen, and the iron is determined in the filtrate, after oxidising with potassium chlorate, by titanous chloride.

(3) After removing the copper with sulphuretted ·hydrogen, the chromium and iron are oxidised with sodium peroxide, and the chromium and iron estimated together.

The following results were obtained :—

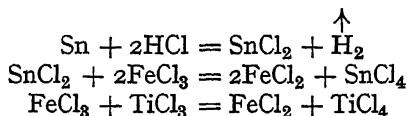|	Amount taken.	Amount found.
Chromium, as Cr_2O_3.	0·02529 grm.	0·02537 grm.
Copper, as CuO . .	0·03186 ,,	0·03180 ,,
Iron, as Fe_2O_3 . .	0·06197 ,,	0·06197 ,,

Tin [2]

The principle involved in the estimation of this metal is not new, being a reversal of the method advocated by Streng for the estimation of ferric iron by means of stannous chloride. The tin is dissolved in strong hydrochloric acid in a flask (provided with a Bunsen valve) at a temperature below 100° C.,[3] and when solution is complete, the contents of the flask are cooled and a known volume (excess) of standard ferric iron (iron alum) is run in. The contents of the flask are then heated for some minutes on the water-bath, while a current of carbonic acid is maintained through the flask to prevent air oxidation. After cooling, potassium sulphocyanide is added, and the excess of iron alum is estimated by titration with titanous chloride. The method gives good results for metallic tin, and is equally applicable for determining the reducing power of commercial stannous chloride.

[1] *J. S. C. I.*, 1909, p. 189.
[2] *Ber.*, 1905, p. 3318.
[3] It was ascertained that by *boiling* the tin with hydrochloric acid serious losses may occur, probably in consequence of some stannous chloride being volatilised when boiled with strong hydrochloric acid. In one case it was shown that boiling for five minutes occasioned a loss of over 4 % of the total tin present.

C

The reactions taking place may be represented by the following schematic equations :—
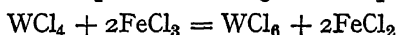
$$Sn + 2HCl = SnCl_2 + H_2\uparrow$$
$$SnCl_2 + 2FeCl_3 = 2FeCl_2 + SnCl_4$$
$$FeCl_3 + TiCl_3 = FeCl_2 + TiCl_4$$

1·1144 grm. of a high-grade commercial pure tin yielded by treatment with nitric acid 1·4146 grm. SnO_2, which calculates out to 99·85 % tin. The same sample analysed in the manner above indicated gave 99·96 and 99·87 % respectively.

Tungsten [1]

As is well known, tungstic acid is reduced to the condition of WCl_4 by energetic reduction with granulated zinc and hydrochloric acid. Otto von der Pfordten [2] has utilised this reaction for the quantitative estimation of tungsten, titrating the reduced solution with permanganate in presence of manganous sulphate. The appearance of a pink colour is coincident with the oxidation back to tungstic acid.

In the new method the same reactions are relied upon, but iron alum is chosen as the oxidising agent, with potassium sulphocyanide as indicator. The titration is thus rendered possible in presence of salts of iron, and can be conducted in even strong hydrochloric acid solution.

The reaction takes place according to the equation—

$$WCl_4 + 2FeCl_3 = WCl_6 + 2FeCl_2$$

The method was tried in the first place on pure dry tungstic acid, the purity of which was ascertained by reducing a known weight in a current of pure dry hydrogen at a temperature of about 600° C.

0·5320 grm. of tungstic acid gave 0·4220 grm. metallic tungsten. The amount required by theory is 0·4219 grm. A known weight of this product was now dissolved in ammonia, the solution acidulated with strong hydrochloric acid and reduced with pure granulated zinc in a flask through which a current of carbon dioxide was maintained.[3] The solution thus obtained was titrated with standard iron alum in presence of potassium sulphocyanide, and gave 99·69 % WO_3.

[1] *Proc. Chem. Soc.*, 1909, p. 227.
[2] *Ber.*, 1883, p. 508.
[3] If this precaution is not taken the WCl_4 very readily suffers oxidation by contact with the air, and the results consequently come out low.

A pure recrystallised tungstate of soda ($Na_2WO_4 + 2H_2O$) titrated in the same way gave the following result :—

	Found.	Calc.
Na_2WO_4	89·36 %	89·06 %
Water of cryst.	10·72 ,,	10·94 ,,
	100·08 ,,	100·00 ,,

Tungsten and Iron [1]

In order to ascertain whether the estimations of tungsten by the new method were in any way affected by the presence of iron, known amounts of pure tungstate of soda were reduced as above in presence of weighed quantities of iron wire. The results given below are stated in terms of metallic tungsten :

	Taken: Grm.		Found: Grm.
Wo	0·0406	. . . .	0·0404
Fe	0·9770	. . . .	—
Wo	0·0203	. . . .	0·0196–0·0197
Fe	1·0100	. . . .	—
Wo	0·0944	. . . .	0·0929
Fe	1·0200	. . . .	—
Wo	0·1303	. . . .	0·1292
Fe	1·0020	. . . .	—

As will be seen, the results are slightly low in all cases.

Molybdenum [2]

By energetic reduction with zinc and hydrochloric acid, molybdic acid and its salts can be reduced to the condition of $MoCl_3$. This compound can be reoxidised by permanganate and other oxidising agents to the condition corresponding to molybdic acid.
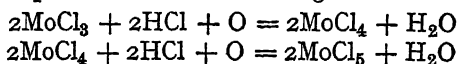
Attempts to base a method of estimating molybdenum upon reduction with zinc and hydrochloric acid, and subsequent titration with iron alum in presence of potassium sulphocyanide proved unsuccessful, since the indicator forms with the reduced molybdenum compound an intensely coloured sulphocyanide which quite obscures the end-reaction with the ferric salt.

A definite end-point was, however, obtained by titrating the

[1] *The Analyst,* 1911, p. 96.
[2] *The Analyst,* 1911, p. 98. The methods for molybdenum and for perchlorates were originally worked out with a view to their utilisation for the indirect volumetric estimation of phosphoric acid and potash respectively, but these objects were not achieved.

reduced molybdenum solution with a standardised solution of Methylene blue. The colour of the former changes from salmon-pink to straw-yellow, then to pale apple-green (due to the formation of $MoCl_5$), and ultimately to the characteristic shade of Methylene blue, this indicating the end-point of the reaction. In this case the oxidation of the $MoCl_3$ does not proceed as far as molybdic acid, as is the case when permanganate is used as the oxidising agent, but only as far as $MoCl_5$. As soon as the oxidation has proceeded far enough to complete the formation of $MoCl_4$, the pale green colour characteristic of the $MoCl_5$ makes its appearance. To obtain the blue colour, exactly twice the volume of Methylene blue has to be added, so that the reaction takes place in two distinct stages—

$$2MoCl_3 + 2HCl + O = 2MoCl_4 + H_2O$$
$$2MoCl_4 + 2HCl + O = 2MoCl_5 + H_2O$$

in which the Methylene blue takes the part of the oxidising agent.

The method was tested on a pure molybdate of ammonia, which was found by the gravimetric method (estimation as lead molybdate) to contain 54·4 % Mo, the amount calculated for the formula $(NH_4)_6Mo_7O_{24} . 4H_2O$ being 54·36 %.

By direct titration with Methylene blue, the following figures were obtained: 54·36; 54·43; 54·39; 54·49 % in different estimations.

The method was also tested on pure molybdic acid, which, when dissolved in ammonia, reduced with zinc and hydrochloric acid, and then titrated with Methylene blue, gave 66·60 % Mo against 66·66 % required by theory.

In all reductions, likewise in the titrations, the reduced molybdenum solution must be kept out of contact with the air, and this is most conveniently effected by passing a current of carbon dioxide through the flask containing the solution. If this precaution is not observed, the results will inevitably come out too low, as is evident from the result of the following experiment :—

A reduced solution of ammonium molybdate titrated as described gave Mo = 54·42 %. In a second experiment, air was drawn for fifteen minutes through the flask containing the reduced solution. The amount of molybdenum found by titration was then only 44·30 %.

The most suitable strength of Methylene blue solution for use in these titrations is $\frac{N}{40}$, or one containing approximately

4 grm. per litre. It is standardised by means of titanous chloride (see p. 64).

For completing the reduction of the molybdenum solution, the apparatus described on p. 70 may be employed with advantage.

Molybdenum and Iron

Ferrous chloride does not reduce Methylene blue in hydrochloric acid solution, and hence the method may be used for the direct estimation of molybdenum in presence of iron, provided that all the iron has been reduced to the ferrous condition. The following results were obtained from mixtures of iron and molybdenum :—

Iron present: Grm.					Molybdenum taken: Grm.					Molybdenum found: Grm.
0·0732	.	.	.	.	0·0348	.	.	.	.	0·0347
0·10 approx.	.	.	.	.	0·0368	.	.	.	.	0·0368
0·15 ,,	.	.	.	.	0·0368	.	.	.	.	0·0367
0·15 ,,	.	.	.	.	0·0368	.	.	.	.	0·0368
1·0 ,,	.	.	.	.	0·0500	.	.	.	.	0·0449

In using this method for the analysis of steel, it is to be noted that the salts of the lower oxides of titanium, tungsten, chromium, and vanadium, also exert a reducing action on Methylene blue.

Vanadium

The volumetric method advocated by Atack [1] is based upon the reduction of vanadium salts from the condition of V_2O_5 by leuco-Methylene blue to the condition of V_2O_4. The Methylene blue thus formed is estimated by titration with titanous chloride. The accuracy of the method was tested on a pure ammonium vanadate, NH_4VO_3, which was found to contain 77·6 % V_2O_5 ; the amount demanded by theory is 77·8 %.

Vanadium, Chromium and Iron in Admixture

The method advocated by Atack [2] for the estimation of vanadium, chromium and iron in a solution containing these three metals is based upon the observation that ferric salts are quantitatively reduced to ferrous and chromic acid to a chromic salt by leuco-Methylene blue, while under the same conditions V_2O_5 is reduced to V_2O_4. The mode of procedure is as follows :—

The solution is oxidised with sodium peroxide, boiled to

[1] *The Analyst*, 1913, p. 98.   [2] (*l.c.*)

destroy excess, acidulated with sulphuric acid and made up to a known volume. An aliquot volume of this is added to excess of leuco-Methylene blue and the amount of Methylene blue formed titrated with titanous chloride. This gives V_2O_5, CrO_3 and Fe_2O_3. Another portion of the oxidised solution is evaporated with concentrated hydrochloric acid to reduce V_2O_5 and CrO_3. The ferric chloride (Fe_2O_3) remaining is estimated by leuco-Methylene blue and back-titration of the Methylene blue formed. Finally V_2O_5 and Fe_2O_3 are estimated together by reducing a fresh portion of the oxidised solution with sulphur dioxide, boiling for a short time, passing a current of carbon dioxide through to displace the sulphur dioxide and running in permanganate until a pink colour is just visible. This solution is then run into excess leuco-Methylene blue and the Methylene blue formed titrated as before. This gives V_2O_5 and Fe_2O_3. Using standard solutions of iron alum, ammonium vanadate and potassium bichromate the following results are recorded :—

	Found: Grm.	Present: Grm.
Vanadium	0·01776	0·01773
Ammonium	0·01045	0·01050
Iron	0·01856	0·01850

Lead and Manganese

L. Moser [1] has found that the addition of titanous chloride solution to lead dioxide leads to the liberation of chlorine, even in the cold. To avoid this loss of chlorine, the lead peroxide is boiled with water, and then an excess of the titanous chloride solution (1 c.c. = 0·0035 to 0·0050 g. Fe) added rapidly, while shaking, in carbon dioxide atmosphere. When solution is complete, 6 to 8 drops of strong potassium thiocyanate are added, and the excess of titanous chloride ascertained by titration with ferric chloride solution. Methylene blue may be also used as indicator. The results agreed with those obtained by the hydrogen peroxide method,[2] but were slightly higher than those obtained by the iodine distillation method of Bunsen as modified by Beck.[3] Red lead may also be analysed by means of titanous chloride, correction being made for the iron content, which is ascertained in a separate portion by boiling with hydrochloric acid to destroy the dioxide before titrating the ferric iron.

The analysis of manganese dioxide is carried out in a similar

[1] *Chem. Ztg.*, 1915, **39**, p. 245.
[2] Schlossberg, *Z. anal. Chem.*, 1902, **41**, p. 741.
[3] *Z. anal. Chem.*, 1908, **47**, p. 465.

manner, but in strong hydrochloric acid solution, and hence Methylene blue, and not thiocyanate, is used as indicator. A large excess of titanous chloride is added to 0·1–0·3 grm. of finely powdered pyrolusite in carbon dioxide atmosphere, an equal volume of concentrated hydrochloric acid added, and the liquid maintained at the boil until all the manganese dioxide has dissolved, which takes a quarter to half an hour for pyrolusite. The results agreed with those obtained by the iodine distillation method.⁵

These methods can only be regarded as means for valuing the oxides named, but not for the estimation of either lead or manganese. For although these metals, when precipitated from aqueous solutions by ammonia or alkali, are supposed to yield by oxidation with oxidising agents like hydrogen peroxide their respective peroxides or the corresponding hydrates these were found to vary in oxygen content, and the results obtained by subsequent reduction with titanous chloride are consequently unreliable. This definite statement is made by the authors as the result of a very long and careful study of the subject. In the case of manganese, reducing agents other than titanous salts gave similar results.

Cobalt

The following process for the volumetric estimation of cobalt is due to H. H. Willard and D. Hall.[1] The cobalt is first converted from the ordinary cobaltous condition to cobaltic hydrate by oxidation with hydrogen peroxide in strongly alkaline solution. The solution is then carefully neutralised and transferred to a known volume of standard titanous sulphate, the excess of the latter being ascertained by titration with permanganate. In place of titanous sulphate, standard solutions of other reducing agents can be employed. The results agree among themselves and with theory.
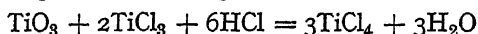
Hydrogen Peroxide and Certain Per-acids [2]

If titanous chloride is added to a solution containing excess of hydrogen peroxide, it is instantly oxidised past the condition of TiO_2 to that of TiO_3, and the solution is coloured more or less intensely yellow. By continuing the addition the colour

---

[1] *J. A. C. S.*, 1922, p. 2219.　　　　[2] *Ber.*, 1905, p. 3314.

will either increase or decrease in intensity according to the amount of peroxide present, but by continued addition it will disappear altogether, according to the scheme—

$$TiO_3 + 2TiCl_3 + 6HCl = 3TiCl_4 + 3H_2O$$

Accordingly, two molecules of titanous chloride ($= 2Fe$) are required for one of hydrogen peroxide.

The titration is carried out by adding standard titanous chloride solution to a known volume of the hydrogen peroxide under examination until the yellow or orange colour at first formed disappears. As the end point is difficult to perceive in artificial light, it was found preferable to add titanous chloride in excess and titrate back the excess with iron alum, using potassium sulphocyanide as indicator.

The method was tested against the recognised methods of estimating hydrogen peroxide, using one and the same sample, with the following results :—

By permanganate.	10·82 vols. oxygen.	
By iodimetry	10·80 ,,	,,
By titanous chloride	10·82 ,,	,,

For the purpose of determining hydrogen peroxide in the ordinary way, the usual clean and exact titration with permanganate would almost invariably be used. But if the peroxide contains oxalic acid or (in the case of partially spent bleach baths) organic matter likely to affect permanganate, the titanous chloride method is preferable.

Addition of excess titanous chloride and back-titration with iron alum was also adopted for the analysis of *perborates*.[1] Sodium perborate yielded, in this way, the following results :—
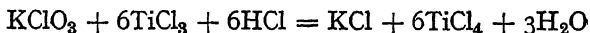
	Found.	Calc. for $NaBO_3.4H_2O$.
B_2O_3	22·56 %	22·72 %
Na_2O	20·08 ,,	20·15 ,,
Water of cryst. . . .	46·80 ,,	46·74 ,,
Available oxygen . .	10·34 ,,	10·39 ,,
	99·78 ,,	100·00 ,,

The *percarbonates* behave like the perborates.

[1] E. K. Farrar, *J. S. D. and C.*, 1910, p. 81 ; Moser and Seeling, *Z. f. anal. Chem.*, 1913, p. 73.

Chlorates [1]

Chlorates are readily reduced in the cold by titanous chloride. Thus, potassium chlorate is quantitatively reduced in a few minutes, according to the equation—

$$KClO_3 + 6TiCl_3 + 6HCl = KCl + 6TiCl_4 + 3H_2O$$

The titration was effected by adding a known amount of the chlorate to an excess of standard titanous chloride solution, allowing to stand for three minutes while a current of carbon dioxide was maintained through the flask, and then titrating back with standard iron alum.
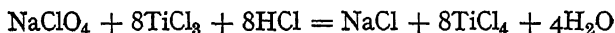
A pure chlorate of potash titrated in this way showed that the reaction is quantitative. The amount found was 99·78 %.

Perchlorates [2]

In dilute aqueous solution the perchlorates are not appreciably reduced by titanous chloride even on prolonged boiling. By a strong solution of titanous sulphate, they are, however, completely reduced, and can be estimated in this way.

The estimation can also be effected by titanous chloride, but only if the latter be used in concentrated solution. The titration of the perchlorate is carried out in fairly strong sulphuric acid solution. The addition of oxalic acid facilitates the reduction in the case of the potassium salt.

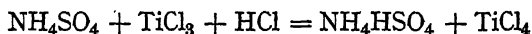The method was tested on pure sodium perchlorate, and the calculation is based upon the equation—

$$NaClO_4 + 8TiCl_3 + 8HCl = NaCl + 8TiCl_4 + 4H_2O$$

The following result was obtained :—

		Calc. for $NaClO_4 + H_2O$
Perchlorate by titration .	86·88 %	87·19 %
Water of cryst. . . .	12·94 ,,	12·81 ,,
	99·82 ,,	100·00 ,,

[1] *J. S. C. I.*, 1908, p. 434.
[2] *Proc. Chem. Soc.*, 1909, p. 229. In a paper on the same subject (*Chem. Ztg.*, 1909, p. 1245) V. Rothmund and A. Burgstaller, while refuting the statements of Stähler (*Chem. Ztg.*, 1909, p. 759) regarding the instability of titanous salts on boiling, confirm the reliability of the process as proposed by Knecht (*l.c.*). They consider, however, that the presence of oxalic acid is superfluous. The process previously proposed by Rothmund for the valuation of perchlorates (*Z. anorg. Chem.*, 1909, p. 108) depended upon the reduction of the perchlorate by means of titanous sulphate followed by the titration of the chlorine by Volhard's method.

Persulphates

Persulphates are readily reduced by titanous chloride in the cold.   The reaction has been found to take place according to the scheme—
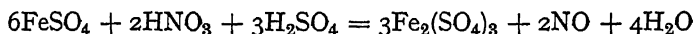
$$NH_4SO_4 + TiCl_3 + HCl = NH_4HSO_4 + TiCl_4$$

For the estimation, excess of titanous chloride is added to a known weight of the persulphate and the solution is back-titrated with standard iron alum.   An ammonium persulphate analysed in this way gave 89·83 % by the titanous chloride and 89·89 % by the iodometric method.

Nitrates

For the estimation of nitrates, titanous chloride may be used in several ways.

In the first place, it can be used in Pelouze's process for ascertaining the amount of ferric iron produced from ferrous sulphate by a known amount of nitrate—

$$6FeSO_4 + 2HNO_3 + 3H_2SO_4 = 3Fe_2(SO_4)_3 + 2NO + 4H_2O$$

10 c.c. of a 1 % solution of pure potassium nitrate were boiled with excess of ferrous sulphate free from ferric salt for ten minutes, in a flask through which a current of carbon dioxide was maintained.   The solution was cooled, and the ferric iron titrated with titanous chloride.

The analysis gave 99·86 % KNO$_3$.

The method has a slight advantage over the original one of Pelouze, in that it is not necessary to weigh the ferrous sulphate. The estimation of the ferric iron by titanous chloride is also more convenient than by stannous chloride as recommended by Streng.

Titanous chloride may also serve for the estimation of nitrates (*e.g.* in sewage) by virtue of the fact that in presence of caustic soda titanous hydrate reduces nitrates quantitatively to ammonia.[1]   The nitrate to be analysed is run into a flask (preferably copper) along with excess of caustic soda, and a few cubic centimetres of titanous chloride are added.   After swirling and allowing to stand for a few minutes, the ammonia is distilled off into decinormal sulphuric acid and estimated in the usual way.   Pure potassium nitrate titrated in this way gave 99·64 %. In place of titanous chloride, titanous sulphate can be used for this estimation.   In either case care should be taken to have a

[1] *J. S. C. Ind.*, 1915, p. 126.

large excess of caustic soda present, for if the solution is allowed to become acid, loss of nitrogen may occur through the escape of NO or N_2O.
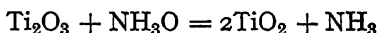
Small quantities of nitrates in water may also be estimated by heating the concentrate on the water-bath with phenol-trisulphonic acid, and then estimating the picric acid (*q.v.*) formed by titration with titanous chloride.[1]

Pure potassium nitrate titrated in this way gave 99·42 %.

Nitrites are also quantitatively reduced to ammonia by the action of titanous hydroxide in presence of excess of caustic alkali. This was shown to be the case by a duplicate experiment with pure crystallised silver nitrite, which yielded in both cases 99·47 % $AgNO_2$.

Hydroxylamine [2]

Hydroxylamine is quantitatively reduced to ammonia by the action of titanous salts, according to the scheme—

$$Ti_2O_3 + NH_3O = 2TiO_2 + NH_3$$

By adding a known amount of hydroxylamine sulphate to excess of titanous chloride and then titrating back the excess of the latter, Stähler (*l.c.*) found 99·65 %, and this was in fairly close agreement with the permanganate titration of the same sample (100·15 %).

Oxygen in Water

For the estimation of dissolved oxygen in water, a modification of the Pelouze process was worked out, in which a known volume of the water was mixed with a small amount of ferrous sulphate free from ferric iron. Caustic soda was added in excess, and after shaking and allowing to stand for some time (out of contact with the air) the contents of the flask were acidulated and the ferric iron titrated in the usual way. The results obtained were in very close approximation to those published by Winkler and Pettersen [3] and by Roscoe and Lunt,[4] as will be seen from the following figures, which show the amounts of oxygen taken up by water from the air expressed in cubic centimetres per litre :—

Temp.	W. & P.	R. & L.	K. & H.
15°	6·94	6·96	6·99
25°	5·69	5·76	5·82

The results obtained by employing manganous hydrate in place of ferrous hydrate were not satisfactory.

[1] F. S. Sinnatt, *Proc. Chem. Soc.*, 1906, p. 255.
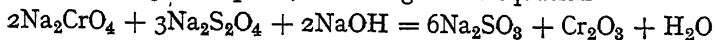[2] *Ber.*, 1904, p. 4732.
[3] *Ber.*, 1891, p. 3602.   [4] *J. C. S.*, 1889, p. 552.

Hydrosulphites

Although Bernthsen's method of titrating hydrosulphites in solution (running the hydrosulphite solution into a standard solution of indigo-carmine until the blue colour disappears) leaves nothing to be desired in point of accuracy and of simplicity, the solid hydrosulphite of soda, which is now manufactured and sold in large quantities, is not so easily dealt with. If dissolved in water it begins almost immediately to decompose, with evolution of sulphur dioxide. By dissolving in dilute caustic soda this decomposition can be avoided, but the salt then absorbs oxygen from the air so rapidly that the result of the analysis may be vitiated by an exposure lasting not longer than a few seconds. These difficulties may be overcome by adding a known weight of the solid hydrosulphite to a known volume (excess) of standard Methylene blue solution contained in a ·flask through which a current of carbon dioxide is maintained. The hydrosulphite instantly reduces its equivalent of Methylene blue, and that which remains unreduced is estimated by titrating with titanous chloride [1] (see under Methylene blue). That the reduction of Methylene blue by hydrosulphite of soda is quantitative was shown by preparing a solution of the hydrosulphite in weak caustic soda and storing this under hydrogen in an apparatus like that used for titanous chloride (see Part III.). This solution was standardised on pure Indigotine. A titration of the Methylene blue acidulated with acetic acid gave a sharp end point, and the result obtained was exactly the same as that obtained by titration with titanous chloride.
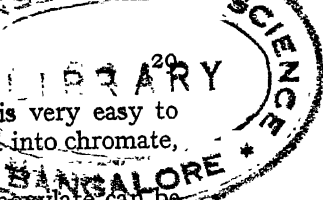
In place of Methylene blue, a standardised solution of indigo extract may be used for the valuation of hydrosulphite of soda. The mode of procedure is the same, and the excess of Indigo may either be determined by titration with standard hydrosulphite or with titanous chloride (see below under Indigo). A solid commercial hydrosulphite of soda gave by titrating the ˙excess of Methylene blue with titanous chloride 87·77 %, and by titrating the excess of Indigo with standard hydrosulphite 87·65 % $Na_2S_2O_4$.

An alternative method [2] is based upon the observation that whereas sulphites are unaffected by boiling with a soluble chromate in presence of caustic soda, a quantitative reduction ensues with hydrosulphite, according to the equation—

$$2Na_2CrO_4 + 3Na_2S_2O_4 + 2NaOH = 6Na_2SO_3 + Cr_2O_3 + H_2O$$

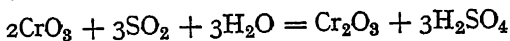[1] *Ber.*, 1907, p. 3319.   [2] *J. S. D. and C.*, 1915, p. 94.

The bright green precipitate thus obtained is very easy to filter. After filtering and washing it is converted into chromate, which is titrated as described on p. 74.

The formaldehyde compound of sodium sulphoxylate can be titrated in a simpler manner by running a solution of a known weight of the compound in 100 c.c. from a burette into a boiling standard solution of Methylene blue until the latter is decolourised.

Estimation of Sulphurous Acid in Sulphites and Bisulphites [1]

This estimation depends upon the reduction of chromic acid by sulphurous acid—

$$2CrO_3 + 3SO_2 + 3H_2O = Cr_2O_3 + 3H_2SO_4$$

and the subsequent estimation of the excess of chromate by titanous chloride.

The accuracy of the method was tested with freshly prepared and crystallised specimens of sodium sulphite $Na_2SO_3 . 7H_2O$ and magnesium sulphite $MgSO_3 . 6H_2O$.
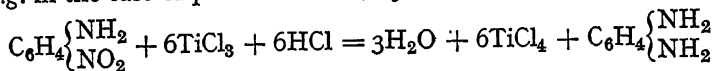
The sodium sulphite (like that employed by Giles and Shearer) contained a small amount of sulphate and gave 99·01 % ; the same sample analysed by the method of Giles and Shearer [2] gave 99·12 %.

The magnesium sulphite was found to be free from sulphate and gave by the new method 99·8 %.

B.—ORGANIC COMPOUNDS

Nitro Compounds [3]

The nitro compounds are quantitatively reduced by titanous chloride in acid solution, and the reduction can be represented, e.g. in the case of paranitraniline, by the following equation :—

$$C_6H_4 \begin{cases} NH_2 \\ NO_2 \end{cases} + 6TiCl_3 + 6HCl = 3H_2O + 6TiCl_4 + C_6H_4 \begin{cases} NH_2 \\ NH_2 \end{cases}$$

In no case could the disappearance of the colour be taken as the end point of the reaction, as it is not sufficiently sharp. The practice invariably followed was, therefore, to add a known

[1] J. S. D. C., 1915, p. 209.
[2] J. S. C. I., 1884, p. 197, and 1885, p. 303.
[3] Ber., 1903, p. 1549.

amount of the nitro compound to an excess of titanous chloride, and after boiling for some minutes in a current of carbon dioxide, to cool the contents of the flask and titrate back the excess of titanous chloride with iron alum, using potassium sulphocyanide as indicator. Nitro compounds which are insoluble in water or in acids (*e.g.* nitrobenzene) may be sulphonated with ordinary or fuming sulphuric acid, while nitro compounds which, like trinitrotoluene, are neither soluble in water nor easy to sulphonate may be dissolved in alcohol and added slowly to the hot solution of titanous chloride contained in a flask through which a current of carbon dioxide is maintained.

The method was shown to give reliable results in the following cases :—

Paranitraniline.—The product crystallised several times from alcohol showed the melting point 147°, and was dried before weighing at 100°. The titration gave—

I. 99·68 %
II. 99·92 ,,

Sodium Salt of Dinitrostilbene Disulphonic Acid.—The salt recrystallised several times from water and dried at 140° gave 99·82 %.

Nitrobenzene.—This compound, which was chemically pure [1] and showed a melting-point of 7° C., was sulphonated by heating for two hours on the water-bath with twenty times its weight of fuming sulphuric acid (20 % SO_3). The titrations gave the following results :—

I. 99·98 %
II. 99·62 ,,

Picric Acid.—The volumetric processes for the estimation of this compound include the direct titration with caustic soda, using phenol phthalëin as indicator [2] and titration with Night blue on the lines laid down by Ch. Rawson for the titration of Naphthol yellow S.[3] By titration with titanous chloride of a sample recrystallised several times from alcohol and showing a melting-point of 122·5°, the following results were obtained :—

I. 100·13 %
II. 100·16 ,,

The homologous compounds *sym.* trinitrocressol and *sym.*

[1] We are indebted for this sample to the late Dr. B. W. Gerland.
[2] Kay, *J. S. D. and C.*, 1888, p. 84.
[3] *Ibid.*, p. 83.

trinitroxylenol are more difficult to reduce than picric acid, but by using a fair excess of titanous chloride and boiling for about five minutes they are completely reduced.

The molecule of picric acid, containing as it does three nitro groups, requires for its reduction eighteen equivalents of titanous chloride, and it is consequently possible to carry out an exact titration with an amount of picric acid not exceeding one milligramme. This estimation represents, therefore, one of the most accurate in volumetric analysis.

m-Dinitrobenzene (m.p. 90°).—This substance is difficult to sulphonate even with fuming acid. The method adopted was to dissolve a known weight of the substance in alcohol, and run this solution into a known volume of standard titanous chloride solution (excess) heated to about 80°. The dinitrobenzene at once separated in a fine state of division, and by boiling the contents of the flask for five minutes while passing a current of carbon dioxide, complete reduction was effected. The contents of the flask were then cooled, and the excess of titanous chloride ascertained in the usual way by titration with standard iron alum. The amount of dinitrobenzene obtained in this way was 100·11 %.

Dinitrotoluene (1.2.4., m.p. 71°) analysed in the same way gave 99·72 %, while dinitronaphthalene (1.8., m.p. 170°) gave 99·74 %.

Trinitrotoluene (1.2.4.6., m.p. 82°), commonly known as T.N.T., is quantitatively reduced by excess of titanous chloride to triamidotoluene. The pure product showed by titration 99·9 %.

The method may also serve for estimating the number of nitro groups in an organic compound.

The behaviour of certain nitro compounds in presence of titanous chloride shows some anomalies. Thus it was found that in presence of an excess of hydrochloric acid α-nitronaphthalene was liable to give low results. Seidler showed [1] that when this compound is reduced in strongly acid solution by means of stannous chloride, the reaction is liable to take place abnormally in that in place of naphthylamine a certain proportion of monochlornaphthylamine results. It has been assumed that a similar action takes place in using titanous chloride in place of stannous chloride.[2] This has now been definitely shown to occur by reducing α-nitronaphthalene with titanous chloride in presence of a very large excess (24 mol.) of hydrochloric acid

[1] *Ber.*, 1878, p. 1201.
[2] T. Callan and J. A. R. Henderson, *J. S. C. I.*, 1922, 1587.
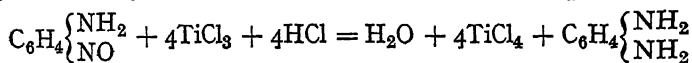
when the reaction resulting in the formation of the $1 \cdot 4$ mono-chlornaphthylamine becomes the main reaction giving, under favourable conditions, a yield of 94% of the monochlor compound.[1] Nitroanisol [2] behaves like α-nitronaphthalene and it is possible that other nitro compounds may be found to behave similarly. On this account Callan and Henderson [3] have recommended the use of titanous sulphate in place of the chloride for the estimation of nitro compounds, as well as for other purposes.

On the other hand, it has been found by T. Henderson and A. H. Macbeth [4] that when picryl chloride, $C_6H_2Cl(NO_2)_3$, is treated with titanous chloride there is not only quantitative reduction of the nitro groups but simultaneous removal of the chlorine from the nucleus.

β-nitronaphthalene when titrated with $TiCl_3$ was found to behave normally even in presence of a large excess of hydrochloric acid.

Nitroso Compounds

Of nitroso compounds, *nitrosodimethylaniline* was found to be quantitatively reduced at 40–$50°$ according to the equation—

$$C_6H_4\begin{Bmatrix}NH_2\\NO\end{Bmatrix} + 4TiCl_3 + 4HCl = H_2O + 4TiCl_4 + C_6H_4\begin{Bmatrix}NH_2\\NH_2\end{Bmatrix}$$

The end point is easily perceived in daylight by the disappearance of the yellow colour.[5]

A titration of a specimen of nitrosodimethylaniline which had been purified by recrystallisation and showed a melting-point of $85°$ C. gave $98 \cdot 88$ %.

It was thought that this reaction might be utilised for the valuation of nitrites, and a number of experiments were carried out with this end in view, the principle adopted being to add slowly a known amount of the nitrite in solution to a cooled solution of dimethylaniline (excess) in hydrochloric acid, and then to titrate the nitroso compound formed. But although satisfactory results were obtained with pure nitrite of soda, it was found that the presence of nitrate (which is the chief impurity) obscured the end point and rendered the method useless for

[1] *J. C. S.*, 1924, p. 1537.
[2] See also N. G. Hurst and J. F. Thorpe, *J. C. S.*, 1915, p. 3934.
[3] *l.c.*
[4] *J. C. S.*, 1922, p. 892.
[5] Salvaterra (*Chem. Zig.*, 1914, p. 90) has suggested a modification of this process for which he claims a sharper end point. He adds excess of titanous chloride, boils and titrates back with standard Methylene blue.

practical purposes. The probable cause of this failure was later recognised in the observation that if titanous chloride is added to a solution of dimethylaniline containing nitric acid, formation of nitroso dimethylaniline occurs through the reduction of the nitric to nitrous acid by the titanous chloride.

Paranitrosophenol (m.p. 123–125°) titrated in the same way gave 99·65 %. Methylene blue may be used as an indicator, but in a good light the end point is sufficiently distinct without.

Nitrosobetanaphthol is best titrated according to Callan (private communication) by first reducing with excess TiCl₃ at 60° and back-titrating with iron alum. A pure specimen titrated in this way gave 99 %.

Benzildioxime when reduced by titanous chloride requires the equivalent of 4H and can be estimated according to Atack [1] by reducing hot with excess titanous chloride and then titrating back with standard Methylene blue. The beta-benzildioxime of m.p. 206–207° gave in this way 99·9–100·2 %. Benzophenonoxime behaves similarly, but the oximes of the fatty series such as acetoxime or dimethylglyoxime could not be analysed in this manner.

Diazo Compounds [2]

If a solution of diazobenzene chloride (benzene diazonium chloride) containing not more than two molecules of hydrochloric acid [3] is titrated with titanous chloride, it is found that the reaction (spot test) with alkaline betanaphthol or H acid ceases after an amount of the reducing agent equivalent to two atoms of hydrogen has been added. It is noticed that a finely divided pale yellow precipitate forms in the solution which rapidly coagulates and rises to the surface as a yellowish-brown scum. The reaction, which results in the formation of the insoluble diazobenzene phenylhydrazide, is quantitative and is expressed by the following equation :—

$$2C_6H_5N_2Cl + 4TiCl_3 + 2HCl = C_6H_5N : N . NC_6H_5 . NH_2 + 4TiCl_4$$

Using pure aniline as starting point, diazotising in the usual way and titrating the cold solution with standard titanous chloride, this reaction gave 100·08 % diazobenzene chloride (expressed in terms of aniline).
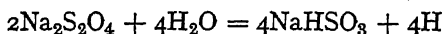
[1] *J. C. S.*, 1913, p. 1319.
[2] *J. S. D. and C.*, 1920, p. 215.
[3] In a solution strongly acidulated with hydrochloric acid, titanous chloride and diazobenzene chloride do not interact.

In place of using H acid as external indicator, it is found preferable to add excess of titanous chloride to the cooled solution and back-titrate with a standard solution of Acid green in presence of sodium tartrate. This colouring matter is quantitatively reduced by titanous tartrate in the cold to a colourless solution but is not reduced by phenylhydrazine [1] or by diazobenzene hydrazide. The quantitative reduction of the diazo compound requires about fifteen minutes in the cold, after which sodium tartrate is added and the back-titration with standard Acid green carried out. In a titration carried out in this way the amount of titanous chloride solution used was $16\cdot37$ c.c. whereas the amount calculated for $2H$ was $16\cdot3$ c.c.

By substituting sodium hydrosulphite for titanous chloride and titrating again throughout at a low temperature it was found that the reduction in hydrochloric acid solution went as far as hydrazine and was quantitative, two molecules of hydrosulphite being required for one molecule of the diazo compound—

$$2Na_2S_2O_4 + 4H_2O = 4NaHSO_3 + 4H$$

The resulting bisulphite takes no part in the reaction.

The method was found inapplicable in the case of paranitro diazobenzene chloride and of " nitrosamine " (sodium salt of paranitro isodiazobenzene). They are more readily reduced than diazobenzene chloride, for in presence of most indicators they are reduced preferentially, whereas preferential reduction was in no case obtained with benzene diazonium chloride. For the titration with titanous chloride in presence of sodium tartrate a great variety of indicators have been tested, but in all cases in which selective action took place, the nitro group was attacked before the indicator was reduced. A back-titration was not possible, as excess of the reducing agent immediately reduces the nitro group.

By adding to the sodium compound an excess of titanous chloride in presence of sodium tartrate and back-titrating the excess with Crystal scarlet, the amount of hydrogen consumed would indicate that reduction had taken place according to the following equation :—

$$NO_2C_6H_4N_2ONa + 12TiCl_3 + 14HCl =$$
$$NH_2C_6H_4NH_2 + NH_4Cl + NaCl + 12TiCl_4 + 3H_2O$$

the analysis working out at $98\cdot4$ % $NO_2C_6H_4N_2ONa$, $2H_2O$.

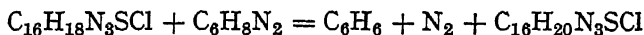Starting with pure paranitraniline, this was diazotised in the

---

[1] Of other colouring matters it was found that Rosinduline G, Rhodamine Safranine and Patent blue A were not reduced by phenyl hydrazine.

usual manner, sodium tartrate added in excess and then titanous chloride in excess. Back-titration with Crystal scarlet showed that the diazo compound had used up 12·04H in place of 12H required by theory.

Reduced in alkaline solution by sodium hydrosulphite with Rosinduline G as internal indicator, the nitrosamine required only 4H, yielding paranitrophenylhydrazine. The percentage worked out at 98·3.
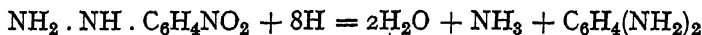
Phenylhydrazine [1]

Although phenylhydrazine is not reduced by titanous salts, it may be oxidised quantitatively by means of a solution of Methylene blue. The reaction is accompanied by evolution of nitrogen and may be represented as taking place as follows :—

$$C_{16}H_{18}N_3SCl + C_6H_8N_2 = C_6H_6 + N_2 + C_{16}H_{20}N_3SCl$$

The Methylene blue is thus decolourised to Methylene white, but as the end point obtained by direct titration is not very easily discerned it is found preferable to add excess of Methylene blue standardised by means of titanous chloride, and back-titrate the latter, after the reaction has gone to completion, by standard titanous chloride. Titrated in this way phenylhydrazine was found in one case to give 99·3 % and in another 99·8 %.

The same reaction has been employed for estimating phenyl-glucosazone. The product is hydrolysed by warming with strong hydrochloric acid and the phenylhydrazine estimated, as described above, in the diluted solution. Phenylglucosazone (m.p. 205°) titrated in this manner gave 99·75 %.

Paranitro phenylhydrazine.[2]—Unlike phenylhydrazine, this compound is readily reduced by titanous chloride, yielding p. phenylene diamine and ammonia—

$$NH_2 . NH . C_6H_4NO_2 + 8H = 2H_2O + NH_3 + C_6H_4(NH_2)_2$$

The titration is effected in hydrochloric acid solution, using excess TiCl$_3$ and, after reduction, titrating back with standardised Crystal scarlet solution. By this method pure p. nitrophenyl-hydrazine (m.p. 157°) gave 99·6 %.

The same principle was applied to the estimation of the p. nitrophenylhydrazine produced by acid hydrolysis of a known weight of acetone p. nitrophenylhydrazone. This gave 78·8 %, while that demanded by theory is 79·3 %.

[1] *J. C. S.*, 1924, p. 1537.
[2] F. Robinson, *J. Manch. Coll. Techn.*, 1913, p. 105.

Dinitrophenylhydrazine (1.2.4) was found, when reduced and back-titrated with iron alum, to require the equivalent of 14H. The ammonia was estimated in the reduction products and was found to agree with the amount demanded by theory (Willson).

Phenylglucosazone

This compound which results when glucose, laevulose, invert sugar, inverted maltose or glucosamine are warmed with phenyl-hydrazine in presence of acetic acid, is almost insoluble in water and sparingly soluble in alcohol and in dilute acetic acid. The substance employed was prepared from pure glucose and showed m.p. 205°. For titration it was dissolved in alcohol and this solution added slowly to an aqueous solution of tartrate of soda (excess) in a conical flask. Excess of standard titanous chloride was run in and the solution boiled for about six minutes in a current of CO_2. The excess of $TiCl_3$ was ascertained by back-titration, after adding excess HCl, with standardised Crystal scarlet solution to the appearance of a red colour. Under these conditions it was found that reduction takes place, as is indicated by Emil Fischer,[1] according to the equation—

$$C_{18}H_{22}N_4O_4 + 6H + H_2O = C_6H_{13}NO_5 + NH_3 + 2C_6H_5NH_2$$

the reduction products being isoglucosamine, ammonia and aniline. The result obtained by this titration was 99·6 %. By titrating back with a standardised solution of Lanacyl blue in place of Crystal scarlet, the result was 99·5 %.

Sugars

The reducing sugars may be estimated volumetrically by means of titanous chloride in two entirely different ways.

According to the first of these, their estimation is effected by ascertaining the extent to which they act as reducing agents in an alkaline medium. This procedure is purely empirical, for the oxidation of a sugar like glucose is a complicated process resulting in the formation of a number of products and the amount of oxygen consumed bears no definite stoichiometric relation to the amount of glucose employed.[2] The oxidising agents in

[1] *Ber.*, 1886, p. 1920.
[2] Willstaetter and Schudel's modification of Romijn's process (*Ber.*, 1918, p. 780) which depends upon the oxidation of glucose by means of a hypoiodite of soda under specified conditions does, however, take place on stoichiometric lines, but is limited to the estimation of the dextrose, laevulose not being affected.

general use are alkaline copper or mercury solutions, but it is now shown that solutions of Methylene blue and other dyestuffs may be employed for the purpose with advantage.

The estimation of glucose and other reducing sugars may be rapidly and accurately effected by boiling in the usual way with a known volume of Fehling's solution, and then estimating the copper in the filtrate from the cuprous oxide by means of titanous chloride.[1] It is of course necessary, in adopting the procedure, to measure the Fehling's solution accurately, and to know exactly the amount of copper that it contains.

The process was tested on a pure recrystallised cane sugar, which was found to contain only traces of ash. A known weight of this was inverted in the usual way by heating with dilute hydrochloric acid, and was then analysed as described above.

Assuming that 0·03464 grm. $CuSO_4 . 5H_2O$ is completely reduced by 0·05 grm. dextrose or 0·047 grm. cane sugar, the following results were obtained :—

I. 100·04 %
II. 100·08 „

It is, therefore, evident that the presence of the oxidation products of the glucose and laevulose had no influence on the accuracy of the copper determinations. It is claimed that the method is more rapid than the usual gravimetric method, while by making up the filtrate from the cuprous oxide to a known volume, and using aliquot parts of this, two or more titrations can be carried out.

The reducing action of glucose in presence of caustic alkali on many dyestuffs is well known and has been taken advantage of in a number of technical processes. The decolourising action of glucose on an alkaline Methylene blue solution is in common use as a qualitative test for the former in urine. Although these reactions have been known and employed for a long time they never seem to have been studied from a quantitative point of view with chemically pure materials.
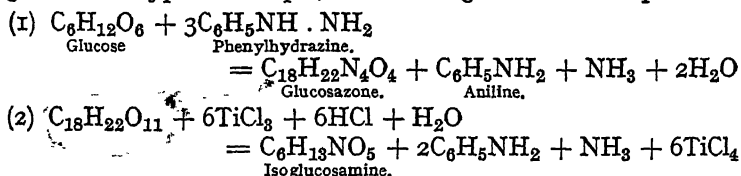
If a solution of Methylene blue is added gradually to a boiling solution of glucose containing caustic alkali, decolourisation by reduction is at first almost instantaneous but gradually slows down during the addition of the dyestuff, so that it becomes difficult to get any definite end point. But if a considerable excess of a standard solution of Methylene blue be added to a

[1] Radlberger and Siegmund (*Oest.-Ung. Z. Zuckerind.*, 1913, p. 34) in commenting on this process, mention that they have found it specially suitable for the estimation of sugar in preserved fruits and in syrups.

known amount of glucose in presence of caustic soda, and the excess of Methylene blue is then ascertained by titration (after acidulating) with titanous chloride, a sharp end point is obtained and it is then found that reduction takes place in definite amount though not in exact stoichiometric proportion. It is remarkable that whereas in using Fehling's solution the extent of the oxidation which takes place is equivalent to less than $2\frac{1}{2}$ O, Methylene blue goes further, the extent to which it oxidises being equivalent to nearly 3 O. Expressed in terms of Fe, this oxidation is equivalent to 0·1833 grm. Fe for 0·1 grm. of glucose or 0·1133 grm. Fe for 0·1 grm. of maltose. The amounts thus ascertained for these two typical sugars bear the same ratio to each other as the figures obtained by means of Fehling's solution.

In carrying out the titration, excess of Methylene blue is added to a solution of 0·04 grm. of glucose in 10 c.c. of water. Caustic soda is then added to the boiling solution, while passing a current of nitrogen ; the flask is swirled, and five seconds after the addition has been made, excess of hydrochloric acid is added and the excess of Methylene blue ascertained by titration with titanous chloride. It is very important to limit the time of the alkaline reaction to five seconds, as if this is exceeded the results become unreliable owing to the resulting decomposition of the Methylene blue base. The process being an empirical one it is not possible to advance any proof of its accuracy.

According to the second method, which might be termed an "absolute" method, the sugar is first converted quantitatively into its osazone, which is then reduced in presence of tartrate of soda by an excess of standard titanous chloride. The excess of the reducing agent is then ascertained, after adding excess hydrochloric acid, by back titration with a standard solution of Crystal scarlet to the appearance of a red colour. Taking glucose as a typical example, the following reactions take place :—

(1) $C_6H_{12}O_6 + 3C_6H_5NH.NH_2$
    Glucose   Phenylhydrazine.
$$= C_{18}H_{22}N_4O_4 + C_6H_5NH_2 + NH_3 + 2H_2O$$
        Glucosazone.   Aniline.

(2) $C_{18}H_{22}O_{11} + 6TiCl_3 + 6HCl + H_2O$
$$= C_6H_{13}NO_5 + 2C_6H_5NH_2 + NH_3 + 6TiCl_4$$
    Isoglucosamine.

It is thus evident that one molecule of glucose requires for its reduction, after conversion into the glucosazone, $6TiCl_3$ which is equivalent to 6 H or 6 Fe.

The reliability of the method was first tested on a sample

of pure phenyl glucosazone.[1] To a solution of 0·02915 grm. of the substance in alcohol, 2 c.c. of a saturated solution of sodium tartrate was added and 50 c.c. of titanous chloride were run in. After the mixture had boiled for six minutes in an atmosphere of CO_2, excess of hydrochloric acid was added and the excess of titanous chloride ascertained by back-titration with Crystal scarlet. This showed 34·2 c.c. excess $TiCl_3$. It follows that 15·8 c.c. of $TiCl_3$ (1 c.c. = 0·001736 grm. Fe) had been consumed in the reduction, and assuming 358 of glucosazone to be equivalent to 6 H or 336 Fe, this give 99·85 % glucosazone.

Since laevulose forms the same osazone as glucose, no further proof was required for this carbohydrate. *Maltosazone*, $C_{24}H_{32}N_4O_9$, gave 99·9 %, and *lactosazone* 99·8 %, using the same method as for glucosazone.

The next requirement in the process was a quantitative conversion of the sugar into its osazone, and this was effected by heating the solution of glucose with a very large excess of pure phenyl-hydrazine dissolved in acetic acid and in presence of sodium tartrate on a water-bath for ten minutes. Under these conditions it was found that the formation of glucosazone as well as the osazones of other sugars became quantitative. The further treatment is the same as that described above.

To test the method, 0·9728 grm. pure glucose was dissolved in water and the solution made up to one litre. Of this solution 25 c.c. were heated with 5 c.c. acetic acid, 1 grm. phenylhydrazine and 1 c.c. of a saturated solution of sodium tartrate on a water-bath for ten minutes. 50 c.c. of standard titanous chloride (1 c.c. = 0·002679 grm. Fe) was run in and the solution boiled on a free flame for one minute, while passing a current of carbon dioxide through the flask. The excess of titanous chloride was ascertained, after acidulating with excess HCl, by titration with a standard solution of Crystal scarlet to the appearance of a red colour and amounted to 33·1 c.c. Therefore 16·9 c.c. of titanous chloride had been used for the reduction of the osazone and as 180 glucose = 336 Fe, the result is equal to 99·76 % glucose.

Other sugars gave the following results [2] :—

Laevulose	99·70 %
Cane sugar after inversion with HCl . .	99·83 ,,
Maltose.	100·03 ,,
,, after inversion	99·9 ,,
Lactose	99·89 ,,
,, after inversion	100·2 ,,
Glucosamine hydrochloride	99·47 ,,

[1] *J. C. S.*, 1924, p. 1545.   [2] *J. C. S.*, 1924, p. 2009.

The method is also applicable to starches and cellulose. The former are first inverted by heating with dilute hydrochloric acid, while for the latter, solution in sulphuric acid of 80 % strength (cold) followed by dilution with water until the strength of the acid is about 20 % and subsequent heating on the water-bath for 20 min. has been found satisfactory.

The " absolute " method is thus seen to be stoichiometrically correct and to give accurate results. It is also rapid, the time required to carry out an estimation of glucose being about 20 min., though if a number of samples were to be done consecutively, this might be still further reduced. No tables are required. In using the method on very dilute sugar solutions (e.g. such as contain o·1 grm. or less of glucose per litre), it becomes necessary to reduce the strength of the standard titanous chloride considerably and it is important to note that in such cases the amount of sodium tartrate added must be reduced in proportion.

Quinones [1]

Quinone is reduced by titanous chloride in presence of hydrochloric acid to hydroquinone, the equation

$$C_6H_4O_2 + 2TiCl_3 + 2HCl = C_6H_6O_2 + 2TiCl_4$$

being quantitative. The reaction takes place at the ordinary temperature, and this fact renders the method possible, for if it were necessary to boil, a considerable loss of quinone would ensue owing to its being extremely volatile with steam.

The titration may be effected in two different ways. According to the first method, the quinone is dissolved in cold water, a known volume of standard titanous chloride is added, and the excess titrated back with iron alum.

According to the second method, the titration may be done directly by using an indicator. The quinone is dissolved as before in cold water, and a drop of weak Methylene blue solution is added. The solution is now titrated directly with titanous chloride, which exercises a selective action on the two substances in solution, reducing the quinone before attacking the Methylene blue. The end point is therefore reached as soon as the blue colour disappears. In consequence of its great intensity, the amount of Methylene blue required to act as indicator is not sufficient to affect the reading.

The methods were tested on a specimen of pure quinone, freshly crysallised from water, and gave the following results :—

Method I. . . . . 99·84 %
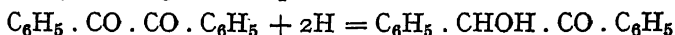Method II. . . . . 99·84 ,,

[1] *Ber.*, 1910, p. 3455.

$$1 \text{ c.c. TiCl}_3 = 0\cdot001639 \text{ grm. Fe}$$
$$285 \text{ C}_{14}\text{H}_7\text{NO}_6 = 336 \text{ Fe}$$
$$1 \text{ c.c. TiCl}_3 = \frac{0\cdot001639 \times 285}{336}$$
$$= 0\cdot001330 \text{ grm. colour.}$$

$0\cdot0209$ grm. sample contain $0\cdot001330 \times 15\cdot6 = 0\cdot02075$ grm.
$$= 99\cdot2 \text{ %.}$$

A nitrogen estimation carried out by the Kjeldahl-Gunning process gave the following result :—

N found $4\cdot83$ %.
Calculated for $\text{C}_{14}\text{H}_7\text{NO}_6$, $4\cdot99$ %.

Azo Dyestuffs [1]

The azo compounds are quantitatively reduced by titanous chloride according to the scheme—

$$\text{R}'.\text{N}:\text{N}.\text{R}'' + 4\text{TiCl}_3 + 4\text{HCl} = 4\text{TiCl}_4 + \text{R}'.\text{NH}_2 + \text{R}''.\text{NH}_2$$

The method was tested in the first instance on *phenyl azo β naphthol*, $\text{C}_6\text{H}_5\text{N}:\text{N}.\text{C}_{10}\text{H}_6\text{OH}$, m.p. 134°. This was sulphonated in the cold with fuming sulphuric acid, and the aqueous solution titrated directly with titanous chloride until decolourised. The titration gave $100\cdot2$ %.

Orange II, $\text{C}_{16}\text{H}_{11}\text{N}_2\text{SO}_4\text{Na} + 5\text{H}_2\text{O}$, gave the following results :—

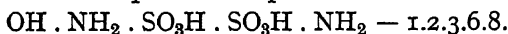|	Calculated.	Found.
Colouring matter	$79\cdot55$ %	$79\cdot49$ %
Water of crystallisation. . . .	$20\cdot45$,,	$20\cdot42$,,
	$100\cdot00$,,	$99\cdot91$,,
Sodium (estimated as sulphate) .	$5\cdot22$,,	$5\cdot12$,,

Crystal scarlet 6 R, $\text{C}_{20}\text{H}_{12}\text{N}_2\text{S}_2\text{O}_7\text{Na}_2 + 7\text{H}_2\text{O}$, gave—

	Calculated.	Found.
Colouring matter	$79\cdot96$ %	$80\cdot01$ %
Water of crystallisation. . . .	$20\cdot04$,,	$19\cdot96$,,
	$100\cdot00$,,	$99\cdot97$,,
Sodium (estimated as sulphate) .	$7\cdot15$,,	$7\cdot11$,,

Fast Acid Magenta.—Azo dyestuff prepared by combining diazobenzene chloride with H acid in alkaline solution, and having the composition $\text{C}_{18}\text{H}_{11}\text{N}_3\text{S}_2\text{O}_7\text{Na}_2 + 6\text{H}_2\text{O}$.

This dyestuff presents special interest in that when reduced it yields a diamido naphthol disulphonic acid—

$$\text{OH}.\text{NH}_2.\text{SO}_3\text{H}.\text{SO}_3\text{H}.\text{NH}_2 - 1.2.3.6.8.$$

[1] *Ber.*, 1903, p. 1549.

which is turned to an intense red by the addition of iron alum in excess. It can therefore either be titrated directly, the end point being coincident with the disappearance of the colour, or excess of titanous chloride may be added, and standard iron alum then run in until the red oxidation product appears. Both titrations give the same result.

The crystallised dyestuff gave the following results :—

	Calculated.	Found.
Colouring matter.	81·92 %	81·6 %
Water of crystallisation ($6H_2O$) .	18·08 ,,	17·8 ,,
	100·00 ,,	99·40 ,,
Sodium (estimated as sulphate) .	7·83 ,,	7·70 ,,

Diamine sky blue (azo dyestuff obtained by combining diazotised dianisidine with H acid in alkaline solution) can be titrated in the same way as the preceding, with this difference, that in using the direct method Rochelle salt should be added.

With *Cotton scarlet*, a dis-azo dyestuff having the composition $C_{22}H_{14}N_4S_2O_7K_2 + 2H_2O$,[1] the amount of titanous chloride required is of course twice as great (calculated on the molecular weight) as for a mono-azo dyestuff. The following results were obtained :—

	Calculated.	Found.
Colouring matter	94·24 %	94·29 %
Water of crystallisation. . . .	5·76 ,,	5·83 ,,
	100·00 ,,	100·12 ,,
Potassium (estimated as sulphate).	12·50 ,,	12·57 ,,

O. Schmidt having pointed out [2] that azo compounds which contain neither free amido nor hydroxyl groups are not reduced by stannous chloride further than to the condition of hydrazo compounds, it was deemed possible that this might also apply, in some cases at least, to titanous chloride.[3] The p_1-nitro p_2-methoxyazo-benzene used by Schmidt was consequently prepared with a view to ascertaining its behaviour towards titanous chloride.

0·25 grm. was dissolved in 250 c.c. alcohol, and of this 10 c.c. were run into excess of titanous chloride, boiled, cooled, and the excess of titanous chloride titrated back with iron alum.

[1] The commercial product is the sodium salt.
[2] *Ber.*, 1905, p. 3202.
[3] The quantitative estimation of Chrysophenin (*J. S. D. and C.*, 1905, p. 3) did not support this.

For the complete reduction of the amount of the compound $CH_3O . C_6H_4 . N : N . C_6H_4 . NO_2$ taken, 0·02179 grm. $TiCl_3$ (expressed in terms of Fe) would be required. The amount found by titration was 0·02177.

On the other hand, it was shown by Grandmougin [1] that *o.* nitrophenyl-azo-phenol treated successively by sodium hydrosulphite and stannous chloride was only reduced to the condition of a triazol.

0·1 grm. of this compound was dissolved in 250 c.c. of alcohol, and of this 25 c.c. were titrated as in the previous case. The amount of titanous chloride (expressed in terms of Fe) required for complete reduction is 0·02304 grm., and the amount found in the titration was 0·02304 grm.

With azo dyes like Benzopurpurin 4 B, which are precipitated by acids from their aqueous solutions, the reduction takes place slowly, even at the boil, and this fact makes it difficult to effect a direct titration. But by the addition of an excess of Rochelle salt to the solution, precipitation of the dyestuff is avoided, and a direct titration can be effected in most cases. The following comparisons show that this is the case :—

	Indirect titration.	Direct titration.
Benzopurpurin 4 B	86·80 %	86·50 %
Erika B	82·12 ,,	82·52 ,,

In the case of yellow azo dyes, the end point is liable to be obscured, in using the direct method, in consequence of the formation of the yellowish-coloured titanous tartrate. For such azo dyes it is preferable to employ the indirect method, which consists in reducing with an excess of titanous chloride and titrating back with iron alum.

The crystallised potassium salt [2] *of Benzopurpurin* 4 B, $C_{34}H_{26}N_6S_2O_6K_2 + 4\frac{1}{2}H_2O$ (obtained from diazotised tolidine and naphthionic acid), titrated in this way gave the following results :—

	Calculated.	Found.
Colouring matter	90·33 %	90·26 %
Water of crystallisation. . . .	9·67 ,,	9·63 ,,
	100·00 ,,	99·86 ,,
Potassium (estimated as sulphate) .	9·44 ,,	9·26 ,,

Brilliant Yellow, $C_{26}H_{18}N_4S_2O_8Na_2 + 3H_2O$.—(From diazo-

[1] *Ber.*, 1906, p. 3929.
[2] The commercial product consists of the sodium salt.

tised diamidostilbene disulphonic acid and phenol.) The crystallised dyestuff gave the following results :—

	Calculated.	Found.
Colouring matter	92·02 %	91·90 %
Water of crystallisation	7·98 ,,	8·00 ,,
	100·00 ,,	99·90 ,,

Chrysophenin,[1] $C_{30}H_{20}N_4O_8S_2K_2 + 6H_2O$.—Diethylether of Brilliant yellow. The well-crystallised salt gave the following results :—

	Calculated.	Found.
Colouring matter	86·80 %	86·56 %
Water of crystallisation. . . .	13·20 ,,	13·20 ,,
	100·00 ,,	99·76 ,,

Erika B,[2] $C_{26}H_{19}N_3O_7S_3K_2 + 8H_2O$.—The crystallised potassium salt gave the following figures :—

	Calculated.	Found.
Colouring matter	82·07 %	82·12 %
Water of crystallisation. . . .	17·93 ,,	17·50 ,,
	100·00 ,,	99·62 ,;

Primuline [3] is not affected by titanous chloride under any known conditions, but the technically important derivative of this dyestuff, viz. the red formed by diazotising it and combining with beta-naphthol, is easily reduced. This red colouring matter was produced in substance, and by recrystallising several times from alcohol, was obtained in the form of microscopic red crystals. Its purity was ascertained by determining the nitrogen and sulphur present, the following results being obtained :—

	Found.	Calc. for $C_{38}H_{22}O_4S_4N_5Na$.
N	9·07 %	9·09 %
S	16·65 ,,	16·7 ,,

The titration was effected by dissolving a known weight of the Primuline red in alcohol and running this solution into water in order to get the dyestuff into a fine state of division. Excess of titanous chloride was then added along with a sufficiency of hydrochloric acid, and the solution was boiled in an atmosphere of carbon dioxide until the red was decolourised. The excess of

[1] The commercial product consists of the sodium salt
[2] The commercial product is the sodium salt.
[3] *J. S. D. and C.,* 1915, p. 241.

titanous chloride was then ascertained in the usual way, by titrating back with iron alum. The amount of colour thus found was 99·6 %.

Tartrazine,[1] $C_{16}H_9O_9N_4S_2K_3 + 5H_2O$.—In its behaviour towards titanous chloride, this colouring matter behaves like an azo-dye, in that it requires 4 H for its reduction. The crystallised potassium salt [2] gave the following results :—

	Calculated.	Found.
Colouring matter	86·07 %	86·11 %
Water of crystallisation. . . .	13·93 ,,	13·98 ,,
	100·00 ,,	100·09 ,,
Potassium (estimated as sulphate) in anhydrous colouring matter .	44·84 ,,	44·67 ,,

Dyestuffs which yield Colourless Leuco Compounds [3]

Under suitable conditions, Indigo (as disulphonic acid) and most of the basic colours (including their sulphonic acids) are quantitatively reduced by titanous chloride, the end point of the reduction being coincident with the disappearance of the colour. The same holds good for the Eosins and rosolic acids.

Methylene Blue, $C_{16}H_{18}N_3SCl$.—This dyestuff is readily decolourised in hydrochloric acid solution by titanous chloride.[4] The direct titration of a sample of pure recrystallised Methylene blue gave the following results :—

Colouring matter	95·96 %
Water at 100°	4·00 ,,
	99·96 ,,

Nitrogen found, 12·44 %. Calculated, 12·57 %.

The zinc chloride double salt which was obtained in well-defined crystals with a bronze reflex by recrystallisation from water, and which has the composition $(C_{16}H_{18}N_3SCl)_2 + ZnCl_2 + H_2O$ gave by titration :—

	Calculated.	Found.
Colouring matter	80·53 %	80·38 %

[1] *J. C. S.*, 1924, p. 1542.
[2] The commercial product is the sodium salt.
[3] *Ber.*, 1905, p. 3319; *J. S. D. and C.*, 1905, pp. 9, 292; *J. C. S.*, 1924, p. 1542.
[4] No Rochelle salt is required for this reduction. If the titanous chloride used contains iron, and Rochelle salt is added previous to the titration, the results will be unreliable, since ferrous salts also reduce Methylene blue in presence of Rochelle salt.

Indigo.[1]—It has already been pointed out (p. 7) that indigotine is reduced by titanous chloride to indigo white. By sulphonating with concentrated sulphuric acid at 90–100°, the indigotine is converted into the water-soluble disulphonic acid, $C_{16}H_8N_2O_2(SO_3H)_2$, and it might have been expected that the aqueous solution of this product would be readily reduced by titanous chloride. Such was, however, not found to be the case, for on adding the reagent to a solution of the dyestuff and boiling, the blue colour, though it first rapidly diminished in intensity, changed to a green, which could only be changed to yellow by prolonged boiling with a very large excess of the reducing agent. Many attempts were made to overcome this difficulty, and after numerous failures it was found that the addition of a considerable amount of Rochelle salt gave rise to a perfectly sharp end point,[2] the colour turning from blue to orange.

The test analysis was made with an indigotine which had been crystallised from nitrobenzene and well washed with alcohol. The product contained 0·18 % of ash and 10·51 % nitrogen (calc. for $C_{16}H_{10}N_2O_2$, 10·68 %). This product gave by titration with titanous chloride 99·5 % indigotine.

In another case the indigotine was crystallised from quinoline and gave 99·28 % indigotine.

A further sample of indigotine kindly supplied by the Badische Anilin and Soda Fabrik, and stated by them to contain 99·50 % indigotine, was found by our method to contain 99·42 %.

It is thus evident that the reduction of indigotine by titanous chloride is quantitative under the conditions given above. The estimation of indigotine in presence of other substances is dealt with in Part III.

Indirubine.—The estimation of this dyestuff may be effected like that of indigotine, viz. by titrating the sulphonated product in presence of sodium tartrate, and in an atmosphere of carbon dioxide until the red colour disappears.

The indirubine used for the test analysis was a synthetic product kindly supplied by the late Dr. T. Sandmeyer, which was recrystallised from alcohol and was found to contain 10·47 % nitrogen (calculated for $C_{16}H_{10}N_2O_2$, 10·68 %). The titration gave 99·60 % indirubine.

Thioindigo Red.—For the test analysis the dyestuff was

[1] *Ber.*, 1905, p. 3318, and *J. S. D. C.*, 1905, p. 292.
[2] When sulphuric acid is present in the solution in large quantity, the addition of Rochelle salt is apt to cause a considerable separation of bitartrate of potash. Sodium tartrate is free from this defect, and can be used with advantage in place of Rochelle salt in this and in other titrations.

crystallised from benzene, being obtained in this way in the form of large brownish-red leaf-shaped crystals. Solution was effected by warming on the water-bath with fuming sulphuric acid, and the titration was done as with indigo, the end point being very sharp. The substance contained 21·42 % S (calculated for $C_{16}H_8S_2O_2$, 21·62 %), and titrated 100·1 % dyestuff.

Isatine.—This substance although of no use as a dyestuff is important as an intermediate product in the manufacture of certain vat dyes. It is readily decolourised in acid solution by titanous chloride forming dioxindole—

$$C_8H_5NO_2 + H_2 = C_8H_7NO_2$$

which oxidises back to isatine on exposure to the air. The titration is effected without the presence of sodium tartrate. By employing a trace of Patent blue as indicator the end point (yellow—green—blue—colourless) is rendered more distinct in artificial light. The titration carried out on a product showing m.p. 201° gave 99·8 %.

Pararosaniline Hydrochloride.[1]—This was prepared in the laboratory from pure pararosaniline, and was obtained in well-defined crystals. A nitrogen determination gave 10·78 %, whereas the amount required by the formula $C_{19}H_{18}N_3Cl + 4H_2O$ is 10·62 %.

The titration was effected with addition of Rochelle salt, and the following result was obtained :—

	Found.	
Dyestuff by titration . . .	81·28 %	
Water of crystallisation . .	18·60 ,,	(calc. 18·28 %)
	99·88 ,,	

A known weight of this dyestuff was sulphonated with fuming sulphuric acid, and the trisulphonic acid titrated in the same way as above. The titration gave 81·38 % dyestuff expressed in terms of pararosaniline hydrochloride.

Crystal Violet.—The dyestuff was purified by recrystallisation from water. A nitrogen determination gave 7·22 %, whereas the amount required by the formula $C_{25}H_{30}N_3Cl + 9H_2O$ is 7·37 %. The results obtained were as follows :—

Dyestuff by titration . . .	71·67 %	
Water of crystallisation . .	28·45 ,,	(calc. 28·44 %)
	100·12 ,,	

[1] *Ber.*, 1905, p. 3318 ; and *J. S. D. and C.*, 1905, p. 292.

Triphenylpararosaniline hydrochloride.—The substance was prepared in the laboratory by phenylating pure pararosaniline, and was purified by recrystallisation from alcohol. A nitrogen estimation gave 7·38 % against 7·6 % calculated for $C_{37}H_{30}N_3Cl$. For the titration, which, like the previous titrations of rosaniline derivatives, was carried out in presence of Rochelle salt, the product was sulphonated with ordinary sulphuric acid at 100° in order to form the soluble trisulphonic acid. The following results were obtained :—

Colouring matter by titration	93·37 %	
Loss at 120° C.	6·89 ,,	

                                                100·26 ,,

Rhodamine B.[1]—With this dyestuff, as also with the Eosines, it is necessary to add alcohol before titrating. If this addition is omitted, the solution becomes turbid on adding titanous chloride (probably in consequence of separation of the leuco compound), and this obscures the end point. The Rhodamine base used for the test analysis formed well-defined cubical crystals, which transmitted a ruby red light and showed a metallic sheen on the surface. A nitrogen estimation gave 5·16 %, while the nitrogen calculated for the formula $C_{28}H_{31}N_2O_3 + 4H_2O$ is 5·45 %.

For the titration, the base was dissolved in hydrochloric acid, and titrated in presence of Rochelle salt and alcohol. The results were as follows :—

Dyestuff by titration . . .	86·87 %	
Water of crystallisation . .	13·20 ,,	(calc. 13·90 %)

                                                100·07 ,,

Eosin A.—This dyestuff was obtained in the form of beautiful red needle-shaped crystals by recrystallising from dilute alcohol. A sodium estimation gave 5·39 %, the amount required for the formula $C_{20}H_6O_5Br_4Na_2 + 10H_2O$ being 5·29 %. The following results were obtained :—

Dyestuff by titration . . .	79·21 %	
Water of crystallisation . .	20·50 ,,	(calc. 20·70 %)

                                                99·71 ,,

Phenolphthaleïn.—In presence of sodium tartrate, this

[1] *Ber.*, 1905, 3318.

                                                                    E

substance is quantitatively reduced by titanous chloride to phenolphthalin :

$$C_{20}H_{14}O_2 + H_2 = C_{20}H_{16}O_2$$

The quantitative character of the reaction was ascertained by titrating the pure product (m.p. 256°), the end point being ascertained by allowing a drop taken out on a glass rod to coalesce with a drop of caustic soda solution, when it will have ceased to give a red colour. The titration gave 99·9 %.

Gallëin.—The pure dyestuff was obtained in the crystallised condition by hydrolysing the tetra-acetate (m.p. 242°) with concentrated sulphuric acid, diluting and allowing to crystallise. The titration is effected in presence of sodium tartrate at 50°, the end point being indicated by the change from magenta to pale yellow—

$$C_{20}H_{12}O_7 + H_2 = C_{20}H_{14}O_7$$

The estimation gave the following result :—

Dyestuff by titration .	.	.	94·93 %	
Water at 110° .	. . . .		4·77 ,,	(calc. for one mol. 4·71 %)
			99·70 ,,	

Malachite Green.—The oxalate was used, and this was purified by recrystallisation from water. A nitrogen estimation gave 5·85 %, while the formula $2C_{23}H_{24}N_2 + 3C_2H_2O_4 + 2H_2O$ requires 6·04 %.

The following results were obtained :—

Dyestuff by titration .	. .	96·55 %
Water of crystallisation .	.	3·40 ,, (calc. 3·60 %)
		99·95 ,,

Tetramethyldiamidobenzhydrol

$(CH_3)_2N . C_6H_4 . CHOH — C_6H_4 . N(CH_3)_2$ (Michler's hydrol)

This compound recrystallised from tetralene showed m.p. 96°. It was dissolved in dilute hydrochloric acid, sodium tartrate added, and the intensely blue solution titrated to decolourisation with titanous chloride in an atmosphere of carbon dioxide. The amount found (based on $C_{17}H_{22}N_2O = 2Fe$) was 99·7 %.

Aurin.—The Aurin prepared from orthocressol and oxalic acid was used, and was obtained in well-defined red crystals by washing the crude product with cold alcohol and then crystallising from alcohol containing ammonia.

The titration was effected in diluted alcohol in presence of Rochelle salt, and gave 99·5 % of the compound $C_{22}H_{20}O_3$.

The method was also tested on a dyestuff of the *Patent blue* series, having the constitution—

discovered by Sandmeyer.[1]   It forms large well-defined dichroic crystals showing a very pronounced metallic sheen.   Though not a commercial article, it is of special interest, as it represents the only dyestuff that we have come across which will precipitate tannic acid, but not gallic acid in presence of sodium acetate.[2] Attempts were made to utilise the dyestuff for the quantitative estimation of tannic acid by adding excess to a known weight of tannic acid, and titrating the excess of dyestuff in the filtrate.   These had, however, to be ultimately relinquished, owing to the sparing solubility of the dyestuff.   An analysis gave the following results : Nitrogen found, 5·88 % ; calculated for $C_{24}H_{26}N_2SO_3$ ($+$ 10·8 % H_2O), 5·93 %.

Dyestuff by titration .   .   .   . 89·14 %
Water at 110° .   .   .   . 10·80 ,,

99·94 ,,

Of dyestuffs which readily yield leuco compounds, but do not belong to the triphenylmethane series, only three, viz. Safranine, Rosinduline, and Meldola's blue, were tried quantitatively, though it is highly probable that other azines, as well as the oxazines, indamines, and indulines, would give accurate results.

Tolusafranine.—The dyestuff used was in the form of large needle-shaped crystals, which were found to contain 13·05 % nitrogen.   The formula $C_{21}H_{21}N_4Cl + 3\frac{1}{2}H_2O$ requires 13·09 %.

By titrating in presence of Rochelle salt, the results were invariably 7 to 8 % too high.   No satisfactory explanation can

[1] *J. S. D. and C.*, 1896, p. 154.
[2] It is assumed by many that gallic acid is not precipitated by basic colours in presence of sodium acetate or weak ammonia, and methods for the quantitative estimation of tannic acid have been brought forward which are based on this assumption.   As a matter of fact, however, all the ordinary basic colours, *e.g.* Magenta, Malachite green, Safranine, Methylene blue, etc., are quantitatively precipitated by gallic acid in presence ·of sodium acetate.   It is noteworthy that while Methylene blue yields a pure blue tannate, the gallate is violet.

be given for this. If, however, bitartrate of soda was used in place of Rochelle salt, the following result was obtained :—

Dyestuff by titration . . . . 86·39 %
Water of crystallisation . . . . . . 13·80 „

100·19 „

Perkins' Mauve.[1]—The dyestuff dissolves in water with an intense red-violet colour which is readily decolourised by titanous chloride, giving a sharp end-reaction ; the original colour at once reappears on exposure to the air.

The following result was obtained :—

Colour by titration . . . . 80·0 %
Loss at 110°. . . . . 16·1 „

96·1 „

The calculation is based on the assumption that the product consists of a phenylated tolu-safranine $C_{27}H_{24}N_4(SO_4)\frac{1}{2}$.[2]

Indoine.—This dyestuff, which is obtained by combining diazotised safranine with betanaphthol, was obtained for analysis in well-defined crystals. A nitrogen estimation gave 12·28 %, while the amount required for the formula $C_{31}H_{26}N_5OCl$ (+ 10·30 % H_2O) is 12·05 %. As the dyestuff contains two chromophores, *i.e.* Safranine and one azo group, the amount of titanous chloride required to reduce the molecule is equivalent to 6 of Fe—

Dyestuff by titration . . . . 89·42 %
Water at 110° . . . . 10·30 „

99·72 „

Rosinduline G.—The colouring matter was purified by recrystallisation from dilute alcohol, and after drying at 140° C. was found to contain 6·55 % N, while that demanded by the formula $C_{22}H_{13}N_2SO_4Na$ is 6·60 %.

The titration was conducted in the usual way, in presence of Rochelle salt, the end point being quite distinct. The following figures were obtained :—

Dyestuff by titration . . . . 99·16 %
Water at 140° . . . . 0·42 „

99·58 „

[1] *J. S. D. C.*, 1921, p. 187.
[2] Fischer and Hepp, *Ber.*, 1888, p. 2620.

Meldola's Blue (New Blue).—This was purified by first extracting the commercial crystallised product with benzene in a Soxhlet, and then recrystallising from water. In this way the dyestuff is obtained in the form of beautiful long, almost black needle-shaped crystals. A nitrogen determination gave 7·49 % N, while that demanded by the formula $C_{18}H_{15}N_2OCl . 3H_2O$ is 7·68 %.

The titration is done without the addition of Rochelle salt, and it is not necessary to heat the solution. The following figures were obtained :—

Dyestuff by titration . . . 84·66 %
Water of crystallisation . . 15·27 ,, (calc. for $3H_2O$
————   14·81 %)
99·93 ,,

Of colouring matters of the Gallocyanine series only Gallo-cyanine itself and Prune were studied quantitatively, and in each case the dyestuff was found to correspond exactly to the established quinonoid formula, in respect to the decolourising action of titanous chloride, two equivalents of hydrogen being required.

The dyestuff known as *Prune* was recrystallised several times from methyl alcohol.

A weighed quantity was dissolved in water, and Rochelle salt was added. This was boiled and titrated directly with titanous chloride. The Prune becomes blue on the addition of Rochelle salt, and this colour is changed by reduction to a pale straw colour.

A titration gave 90·23 %.

Water at 100° = 9·56 %. Total = 99·8.

Another estimation of a sample of the Prune dried at 110° gave 100·05 %.

A nitrogen estimation of this product gave 7·34 %. Calculated for $C_{16}H_{15}N_2O_5Cl$ 7·20 %.

Gallocyanine (the diethyl compound), recrystallised in the same way as Prune, titrated with titanous chloride, gave 84·22 %.

A nitrogen estimation by the Kjeldahl process gave the following result :—

Found, 8·32 %. Calculated for $C_{17}H_{16}N_2O_5$, 8·54 %.

The product, dried to constancy at 100°, lost 14·00 %. Total = 98·2 %.

Alizarin [1]

One of the most important of dyestuffs, the time-honoured Alizarin, was not included in the earlier work, and in spite of numerous endeavours, it was thought that it would not be possible to estimate this compound by reduction owing to the lack of a suitable solvent.   But after experimenting for some time with a sample of chemically pure Alizarin, it was found that the estimation could be accomplished in a comparatively simple manner.   A known weight of this substance was dissolved in alcohol, to an aliquot part of the solution titanous chloride solution in excess was added, and the mixture was boiled, giving rise to an intense blue-green colouration.[2]

On titrating back with iron alum, the blue-green changes to yellow, and this indicates the end point.   It was found that the equivalent of four atoms of hydrogen was thus required, which would correspond to the reduction of the Alizarin—

$$\text{(structure: anthraquinone with } CO, CO, OH, OH)$$

to the desoxyalizarin—

$$\text{(structure: with } COH, OH, OH, CH)$$

described by Roemer.[3]   It appears to be probable that the intense blue-green colour is due to the formation of a compound of the titanous chloride with the desoxyalizarin, the end point arriving as soon as the former has been completely converted into the titanic salt by the addition of iron alum.

Anthrapurpurin and Flavopurpurin were found to behave exactly like Alizarin in this respect, four atoms of hydrogen being required in each case.   With Alizarin orange (betanitroalizarin), however, reduction could only be effected as far as amidoalizarin,

---

[1] *J. S. D. and C.*, 1915, p. 241.
[2] Besides being shown by Alizarin, Alizarin S, Flavopurpurin and Anthrapurpurin, this characteristic colouration is shown by the alpha amido- and oxy-anthraquinones, quinizarin, anthrarufin alpha amido-alizarin and purpurin, but not by anthraquinone, the beta amido- and oxy-anthraquinones, beta nitroalizarin, nor by anthragallol.
[3] *Ber.*, **14**, 1259.

the nitro group alone being reduced.   No satisfactory explanation of this anomaly has hitherto suggested itself.

Alizarin black, which, according to the researches of Schunck and Marchlewski,[1] is a dioxynaphthoquinone—

was found to behave towards titanous chloride as a true quinone, in that it requires two atoms of hydrogen for its reduction, as against four for the di-ketones like Alizarin.   The titration of this dyestuff adds further proof to the correctness of the formula established by these investigators.

Alizarin S can be titrated like alizarin.   The pure crystallised sodium salt gave the following result :—

Colouring matter .   .   .   .   94·60 %
Water at 110° .   .   .   .   .   5·11 ,,   (calc. for $5H_2O$ 5 %)

                          99·71 ,,

Na as sulphate in anhydrous salt   .   20·64 % (calc. 20·76 %)

The estimation of Alizarin, Anthrapurpurin, and Flavopurpurin is conducted in the following manner :—

A known weight of the substance dissolved in alcohol is run into a conical flask into which carbon dioxide is passed, and boiled with about 10 c.c. of a 20 % solution of Rochelle salt. A measured excess of titanous chloride is added, the mixture is again boiled, and the excess of titanous chloride is determined by titrating directly with iron alum solution.   All three compounds show intense blue-green colourations with excess of titanous chloride, but this colour is destroyed when the last trace of titanous salt has been oxidised with iron alum.   The disappearance of the blue-green colour indicates the end of the reaction, and no other indicator is required.

Analysis of Pure Crystallised Alizarin.—0·4780 grm. was dissolved in alcohol and made up to 500 c.c.   To 50 c.c. of this solution Rochelle salt was added, and 50 c.c. $TiCl_3$; 22·9 c.c. of iron alum was required to destroy the blue colour.

22·9 c.c. iron alum = 24·9 c.c. $TiCl_3$

[1] *Ber.*, 1894, p. 3462.

and $50 - 24\cdot9 = 25\cdot1$ c.c. $TiCl_3$ were used in reducing the Alizarin.

$$1 \text{ c.c. } TiCl_3 = 0\cdot001773 \text{ grm. Fe}$$
$$240 \text{ } C_{14}H_8O_4 = 224 \text{ Fe}$$

Therefore 1 c.c. $TiCl_3 = \dfrac{0\cdot001773 \times 240}{224}$

$$= 0\cdot001899 \text{ grm. } C_{14}H_8O_4$$

and $0\cdot001899 \times 25\cdot1 = 0\cdot04766$ grm. $= 99\cdot7$ %.

Ultimate analysis gave the following results :—

$0\cdot1842$ grm. taken gave $0\cdot4741$ grm. CO_2, and $0\cdot0532$ grm. H_2O.

	Found.	Calc. for $C_{14}H_8O_4$.
C	70·14 %	70·00 %
H	3·21 ,,	3·33 ,,

Analysis of Pure Anthrapurpurin.—$0\cdot246$ grm. was dissolved in alcohol and made up to 250 c.c. ; 50 c.c. was titrated in the same way as Alizarin with 50 c.c. $TiCl_3$; $23\cdot75$ c.c. iron alum was required in titrating back, this being equal to $25\cdot8$ c.c. $TiCl_3$ in excess.

Therefore $24\cdot2$ c.c. was required to reduce the Anthrapurpurin

1 c.c. $TiCl_3 = 0\cdot001773$ grm. Fe.

$$256 \text{ } C_{14}H_8O_5 = 224 \text{ Fe}$$

Therefore 1 c.c. $TiCl_3 = \dfrac{0\cdot001773 \times 256}{224}$

$$= 0\cdot002026 \text{ grm. } C_{14}H_8O_5$$

and $0\cdot0492$ grm. sample contains $0\cdot002026 \times 24\cdot2 = 0\cdot04903$ grm.

$$C_{14}H_8O_5 = 99\cdot65 \text{ %.}$$

Ultimate analysis—

$0\cdot1657$ grm. taken gave $0\cdot3979$ grm. CO_2, and $0\cdot0467$ grm. H_2O.

	Found.	Calc. for $C_{14}H_8O_3$.
C	65·48 %	65·62 %
H	3·13 ,,	3·12 ,,

Analysis of Flavopurpurin.—$0\cdot2425$ grm. was dissolved in alcohol and made up to 250 c.c. ; 50 c.c. was titrated in the same way as the previous samples with 50 c.c. $TiCl_3$.

$30\cdot9$ c.c. iron alum were required to titrate back, and this corresponds to $29\cdot2$ c.c. $TiCl_3$ in excess.

And $50 - 29\cdot2 = 20\cdot8$ c.c. $TiCl_3$ was required for reduction.

$$1 \text{ c.c. } = 0\cdot002042 \text{ grm. Fe}$$
$$256 \text{ } C_{14}H_8O_5 = 224 \text{ Fe}$$

Therefore 1 c.c. $TiCl_3 = \dfrac{0\cdot002042 \times 256}{224}$

$$= 0\cdot002334 \text{ grm. } C_{14}H_8O_5$$

and 0·04849 grm. sample contains 0·002334 × 20·8
$$= 0·04854 \text{ grm. } C_{14}H_8O_5 = 100·1 \text{ \%.}$$
Ultimate analysis—

0·1842 grm. taken gave 0·4440 grm. CO_2, and 0·0497 grm. H_2O.

	Found.	Calc. for $C_{14}H_8O_3$.
C	65·74 %	65·62 %
H	3·00 ,,	3·12 ,,

Alizarin Black (dioxynaphthoquinon) can be estimated quantitatively by the method used in the case of Alizarin, etc., but the end of the reduction with titanous chloride can easily be determined in the direct titration, when the last trace of blue has been destroyed and the solution becomes yellow. By adding excess of titanous chloride and titrating back with iron alum the same results were obtained.

A preparation of Alizarin black recrystallised from benzene gave the following results : 0·0994 grm. was dissolved in alcohol, Rochelle salt was added, and the boiling solution was titrated directly with titanous chloride. This required 31·7 c.c. $TiCl_3$.

$$1 \text{ c.c. } TiCl_3 = 0·001834 \text{ grm. Fe}$$
$$190 \ C_{10}H_6O_4 = 112 \text{ Fe}$$
$$\text{Therefore } 1 \text{ c.c. } TiCl_3 = \frac{0·001834 \times 190}{112}$$
$$= 0·003127 \text{ grm. } C_{10}H_6O_4$$

and 0·0994 grm. sample contain 0·003127 × 31·7 = 0·09913
$$= 99·75 \text{ \%.}$$
Ultimate analysis—

0·1477 grm. gave 0·3410 grm. CO_2 and 0·0412 grm. H_2O.

	Found.	Calc. for $C_{10}H_6O_4$.
C	62·97 %	63·16 %
H	3·10 ,,	3·16 ,,

In carrying out the estimation of Alizarin orange it was found necessary to adopt the method which has been described on a previous page for the estimation of nitro-compounds, or to titrate with excess of titanous chloride in the presence of Rochelle salt, cool, acidify with hydrochloric acid, and titrate back with iron alum, using potassium sulphocyanide as indicator.

Colouring Matters in Dyed Cotton Fabrics [1]

Indigo.—The principle of the method is based upon the observation that when indigo-dyed cotton is treated with an 80 % solution of sulphuric acid at about 40° C., the cellulose is rapidly hydrolysed, passing into solution, while the indigotine is converted into sulphate, $C_{16}H_{10}N_2O_2 . 2H_2SO_4$. On diluting with water, the indigotine sulphate is instantly hydrolysed with precipitation of indigotine, the products of the cellulose remaining in solution. The indigotine is filtered through a Gooch crucible containing silica or asbestos, washed, dried, sulphonated, and titrated as usual with titanous chloride.

In order to test the method, 7 grms. of cotton yarn and 0·2 grm. of an indigotine of 99·5 % strength were dissolved together in an 80 % solution of sulphuric acid, and the estimation carried out as indicated above. A sharp end point was obtained in the titration, and the amount of indigotine found was 0·1984 grm. in place of 0·1990. The experiment repeated gave 0·1979 grm.

The method was further tested against the acetic acid extraction method of Brylinski (extraction in Soxhlet with glacial acetic acid) on a medium shade of indigo, dyed on bleached cloth, with the following results :—

New method .   .   .   .   .   .   1·43 % indigotine
Brylinski's method   .   .   .   .   1·48 ,,   ,,

The only colour commonly used along with Indigo in cotton dyeing that was found to interfere with the accuracy of the method was manganese bronze, which, if present, may destroy the greater part of the Indigo in the first operation. If found to be present, it can, however, be readily removed by treatment with bisulphite of soda.

Alizarin.[2]—The method adopted was to dissolve a known weight of the fabric, cut up into small pieces, in 80 % sulphuric acid, pour the solution into water and filter through a Gooch crucible containing asbestos fibre. The precipitate was dried, dissolved in alcohol, and in this solution the Alizarin was estimated as described on p. 55. Since Alizarin precipitated in this manner is not entirely insoluble in water, it is necessary to titrate also the filtrate from the diluted sulphuric acid solution and to add the figure thus obtained to that obtained in the first titration.

[1] *J. S. D. and C.*, 1905, p. 3.
[2] W. N. Leigh, *J. S. D. and C.*, 1916, p. 205.

To ascertain the reliability of the method, 16 grms. cotton yarn mordanted for Turkey red but fixed or " dunged " in phosphate instead of arseniate of soda [1] were dyed with 0·236 grm. chemically pure Alizarin, which produced a fairly full Turkey-red shade. The dyed yarn was dried, cut up and dissolved in 80 % sulphuric acid and the Alizarin estimated by titration with titanous chloride. The Alizarin from the washings and that remaining on the sides of the dye-bath was estimated in like manner and these figures are included in the total. The following result was obtained :—

$$\begin{aligned}
\text{Alizarin taken} \quad . \quad . \quad . \quad . \quad . \quad &\text{0·236 grm.} \\
\text{,,} \quad \text{found} \quad . \quad . \quad . \quad . \quad &\text{0·239 ,,}
\end{aligned}$$

Direct Cotton Colours.—The estimation of direct azo dyes in dyed cotton yarns or fabrics can be effected by indirect titration. The mode of procedure is to boil the weighed amount of dyed cotton in dilute hydrochloric acid with an excess of titanous chloride in an atmosphere of carbon dioxide until the colour has been destroyed, and then titrate the excess of titanous chloride with iron alum.

The method was tested by dyeing bleached cotton with a known amount of a direct colour, and estimating separately the amount of colour on the fibre and that left in solution. The following results were obtained :—

<div align="center">Benzopurpurin 4B.</div>

Amount of dyestuff taken	0·10000 grm.
Dyestuff in solution	0·04765 ,,
,, on fibre	0·05230 ,,
	0·09995 ,,

<div align="center">Chrysophenin.</div>

Amount of dyestuff taken	0·05000 grm.
Dyestuff in solution	0·03622 ,,
,, on fibre	0·01399 ,,
	0·05021 ,,

<div align="center">Erika B.</div>

Amount of dyestuff taken	0·05000 grm.
Dyestuff in solution	0·03682 ,,
,, on fibre	0·01334 ,,
	0·05016 ,,

[1] It was not found possible to estimate the Alizarin in Turkey red containing arsenic by means of titanous chloride, as the arseniate present materially affects the titration, giving too high results.

Primuline red[1] may be estimated in dyed cotton material by the same process as that used for a direct cotton colour (see p. 59). A full shade was found in this way to contain about 2 % of actual dyestuff.

It was also found possible to estimate in a similar way a basic colour like Methylene blue dyed on cotton mordanted with tannic acid and tartar emetic. In titrating back with iron alum the end point is marked by the permanent return of the blue.

Amount of dyestuff used . . . . . 0·08450 grm.

Dyestuff, in solution . . . . . . 0·00044 ,,
   ,,   on fibre . . . . 0·08419 ,,

                              0·08463 ,,

Estimation of the Degree of Mercerisation in Cotton Yarns

Cotton which has been mercerised is known to possess a greater affinity for colouring matters than before mercerising, and experience has shown that the amount of a colouring matter like Benzopurpurin 4B which mercerised cotton will take up in dyeing, is in a sense proportional to the strength of the caustic soda which has been used in mercerising. By dyeing the mercerised cotton along with cotton mercerised with known strengths of caustic soda in one and the same bath with an excess of Benzopurpurin 4B, and then estimating the amount of dye-stuff on the fibre in each case, it is possible to arrive at a rough estimate of the strength of caustic soda that has been used in mercerising the sample in question. Regarding the limitations of the process, see p. 114.

Cellulosic Substances

It is well known that cotton and other cellulose material which has suffered damage through the action of acids or oxi-dising agents acquires reducing properties. In his work, *Die Chemie der Cellulose*, Schwalbe describes in detail a method of estimating the reducing values of such cellulosic substances by means of Fehling's solution. Broadly speaking, the mode of procedure adopted is to boil a definite weight of the material in a known volume of Fehling's solution and then estimate the

[1] *J. S. D. and C.*, 1915, p. 241.

copper which has been precipitated on the material as cuprous oxide by dissolving in nitric acid and ascertaining the amount of copper present by the electrolytic method. A complication arises, however, in consequence of a certain proportion of the copper being firmly fixed by the fibre in the blue or cupric condition and in order to ascertain the proportions of cuprous and cupric copper, Schwalbe carries out a blank experiment on the material under examination in the cold, and is thus able to determine the amount of copper fixed in the cupric condition. The cupric copper subtracted from the total copper gives the " copper number," *i.e.* the number of grams of copper precipitated (reduced) as cuprous oxide by 100 grms. of the material.

It has been suggested as an alternative [1] to accelerate the estimation of the cuprous copper by adding the material, after boiling in Fehling's solution and washing, to a solution of iron alum acidified with sulphuric acid and to estimate the amount of ferrous sulphate formed (according to the method described by Schwarz for sugar analysis). The estimation of the copper absorbed may also be effected by titrating the copper left in an aliquot part of the Fehling's solution by means of titanous chloride. The figure obtained in this way represents, however, the total cuprous and cupric copper in the material. By subtracting from this, the figure obtained by the permanganate titration the " copper hydrate number " may be ascertained.

Another alternative suggested is to dispense altogether with the use of copper and employ an excess of a reducible dyestuff such as Rosinduline B, in which a known weight of the material is boiled in presence of caustic soda and in an atmosphere of hydrogen. The unreduced dyestuff is then estimated, after acidulating, with titanous chloride. The results were somewhat low as compared with those obtained by the copper process.

It should be pointed out that exposure of the cellulosic material, previous to the estimation, to the action of caustic alkalies is liable to alter its reducing power to such an extent as render these estimations futile.

A method for the estimation of cellulose is described under *Sugars (q.v.).*

[1] *J. S. D. and C.,* 1920, p. 255.

PART III

DETAILS OF ANALYTICAL METHODS

Preparation of the Solution of Titanous Chloride and the Apparatus used for storing it

EXPOSED to the air both titanous chloride and sulphate rapidly take up oxygen even at the ordinary temperature and lose their reducing strength. Any results obtained without taking the precaution of preventing air oxidation are therefore valueless.

The solution of titanous chloride for use in the volumetric processes described in this book is prepared and stored in the following way :—

50 c.c. commercial titanous chloride (20 % solution) are boiled for about a minute with 100 c.c. concentrated hydrochloric acid in a small flask. The mixture is then cooled and made up to about 2¼ litres in the storage bottle A (see Fig. 1). The solution should occupy the entire capacity of the bottle up to the neck, and should be thoroughly mixed by shaking. The lower outlet of the storage bottle is fitted with a rubber stopper, through which a piece of glass tubing passes. This tubing is bent downwards, and is connected to a bead valve, D^1, which consists of 1½ in. of rubber tubing in the middle of which a piece of glass rod ¼ in. in length, rounded off at each end, is inserted. This and a long piece of glass tubing is used to connect the storage bottle to a side opening in the narrow part of the burette below the graduation mark (50 c.c.). The outlet from the burette consists of a bead valve, D^2, similar to that previously described, and a drawn-out glass delivery tube. The stopper in the top of the storage bottle has two holes. One of these is fitted with a glass tube leading to the top of the burette, and through the other a tube leads to the small hydrogen generator (C). The latter consists of a glass cylinder half filled with a mixture of equal parts hydrochloric acid and water, into which dips an inner

62

tube contracted at the bottom to a narrow aperture, and fitted at the top with a rubber stopper with a hole to receive the tube leading into the storage bottle. This inner tube is filled with ordinary granulated zinc, which is attacked by the hydrochloric acid as soon as the bead valve D^2 is opened, causing a flow of hydrogen which ceases automatically when the bead valve is closed again. The opening of the valve is effected by drawing the rubber tubing from one side of the glass bead by pressure between finger and thumb. The best method of expelling all air from the apparatus is to open the valve D^1, allowing the titanous chloride to flow into the burette and as far as possible up the tube above, then drawing this off entirely by opening the valve D^2 and allowing the hydrogen to escape for some minutes. After this the apparatus is ready for general use.[1]

FIG. 1.

Experience has shown that when the storage bottle containing the dilute titanous chloride solution is freely exposed to direct sunlight, the strength of the solution runs down more rapidly than when it is kept out of contact with the sun. The reason for this has not been ascertained, but it is conceivable that it may be due to a slow photo-chemical decomposition of water by titanous chloride, with liberation of hydrogen and formation of titanic chloride.

If any deposit forms on the glass parts of the apparatus, it can be most effectively removed, before the storage bottle is refilled, by means of a 1 % solution of hydrofluoric acid. The rubber stoppers should be cleaned and softened, from time to time, by wiping with a cloth soaked in toluene.

[1] Subsequent to the publication of the first edition of this book, several modifications of this apparatus have been described. The modifications suggested do not, however, offer any particular advantages. The apparatus as described has so far proved very satisfactory, though it is not denied that it might be improved, especially with regard to economising bench space.

Standardisation of the Solution

The standardisation is best effected with pure ferrous ammonium sulphate. 3·5 grms. of this substance are dissolved in water, and about 100 c.c. 5N sulphuric acid are added. The solution is then made up to 250 c.c. in a graduated flask. 25 c.c. of this solution are carefully oxidised with potassium permanganate of about $\frac{N}{50}$ strength until a faint pink colouration is obtained. A large excess of potassium sulphocyanide is then added, and the ferric iron titrated with titanous chloride until the red colouration due to ferric sulphocyanide entirely disappears. In this connection, it is very important to use a large excess of potassium sulphocyanide as indicator, for the end reaction is thus rendered much sharper. If after oxidation, 25 c.c. of the iron solution should require, for example, 26·3 c.c. titanous chloride to reduce it, then 1 c.c. $TiCl_3 = 0·00191$ grm. Fe.

In place of potassium sulphocyanide, Methylene blue [1] may conveniently serve as indicator in these titrations, for it has been observed that when titanous chloride is added to a solution of ferric sulphate containing Methylene blue, there is selective action, in that the whole of the ferric iron is reduced before the Methylene blue. Since Methylene blue uses up titanous chloride in becoming decolourised, the amount used as indicator should only be sufficient to tinge the solution a very pale blue. Its tinctorial power is however so great that when employed as indicator the amount used has no appreciable influence on the titration. It is obvious that certain other dyestuffs might be applied similarly as indicators, but it is doubtful whether any of these would offer advantages over Methylene blue. The only disadvantage experienced in the use of this indicator is the time (2 to 3 seconds) required for its decolourisation when nearing the end point, in titrating at the ordinary temperature. But if the titration is effected at about 35°, the end point is sharp and instantaneous. Lauterbach [2] has succeeded in overcoming the disadvantage alluded to by adding a small amount of salicylic acid to the liquid to be titrated. This results in a sharp and instantaneous end point being obtained at the ordinary temperature. The authors have verified this result, but instead of adding a weighed amount of salicylic acid to the liquid to be

[1] *Ber.*, 1907, p. 3819.
[2] *Ber. d. 7ten. Internat. Verg. d. Chem.-Kol.*, 1922, p. 33.

titrated as suggested by Lauterbach, find it more convenient to add one drop of a 10 % solution of salicylate of soda. No satisfactory explanation of the activating influence of salicylic acid on this reaction has hitherto been advanced.

Other Special Reagents

Iron alum.—In order to avoid the necessity of weighing and oxidising ferrous ammonium sulphate with permanganate for every standardisation of the titanous chloride, it is best to prepare a large volume (about 10 litres) of iron alum containing about 14 grms. per litre, and strongly acidified with sulphuric acid until the solution assumes a pale straw colour. If the sulphuric acid is not present in considerable excess, the solution is liable to become turbid and to deposit after a time brown basic ferric sulphate. By measuring the exact volume of standard titanous chloride solution required to reduce 25 c.c. of this iron alum solution, using ammonium sulphocyanide as indicator, its strength is determined, and as it will retain the same strength for an indefinite period, if stored in a well-stoppered vessel, this iron alum solution may be used in all subsequent cases for standardising the titanous chloride solution, as well as for back-titrations.

Ammonium sulphocyanide.—This salt serves as indicator for ferric salt and is preferred to the potassium salt for reasons of economy. It is employed as a 20 % solution and in any titration of ferric salt must be present in an amount which is considerably in excess of what would be required to produce the ferric sulphocyanide. Heating or strongly diluting the solution is apt to decolourise the ferric sulphocyanide. It cannot be used in presence of strong oxidising agents such as chromic acid, by which it is converted into the insoluble yellow persulphocyanogen.

Tartrate of soda.—A saturated solution of this salt—

$$C_4H_4O_6Na_2 . 2H_2O$$

is now preferred by the authors to Rochelle salt—

$$C_4H_4O_6NaK . 4H_2O$$

for all titrations in which the presence of a soluble tartrate is required. Using Rochelle salt in excess, the formation of tartar, $C_4H_5O_6K$, is inevitable. This separates out sometimes in such quantities as to interfere with the titration either by causing bumping, when boiling is necessary, or for other reasons. By using a saturated solution in place of a dilute one, the total

F

volume of the liquid is not materially increased by the addition of the necessary amount of tartrate.

Methylene blue.—This dyestuff, which in the pure state has the composition $C_{16}H_{18}N_3SCl$, or, in the form of its beautifully crystallised zinc chloride double salt—

$$2C_{16}H_{18}N_3SCl + ZnCl_2 + H_2O$$

comes into the market in varying degrees of strength and purity. Although some of the commercial products are sufficiently pure for titration purposes, others are apt to contain small amounts of impurities (*e.g.* Methylene red) which interfere with the delicacy of the end point. It is therefore preferable to employ the more reliable " medicinal " Methylene blue which is sufficiently pure for all purposes.

Methylene blue dissolves in water to an intensely blue solution, the colour being still distinct in extreme dilution. By the action of reducing agents such as titanous salts, it is readily reduced to the colourless Methylene white—

$$C_{16}H_{18}N_3SCl + H_2 = C_{16}H_{20}N_3SCl$$

which re-oxidises at once in contact with the air to Methylene blue.

Solutions of Methylene blue standardised by means of titanous chloride may be employed with advantage in several volumetric estimations (*e.g.* titanium, phenylhydrazine).

On the other hand, Methylene blue serves as a useful indicator in certain oxidation and reduction titrations. Thus, it may be used in place of ammonium sulphocyanide in the titration of ferric iron, quinones, etc.

Crystal scarlet $(C_{20}H_{12}N_2S_2O_7Na_2+7H_2O)$. — The standardised solution of this dyestuff is useful in certain back-titrations (*e.g.* paranitro phenylhydrazine, phenylglucosazone). The crystallised commercial product is usually sufficiently pure ; if not, it can easily be purified by recrystallisation from water. By titanous chloride it is reduced quantitatively to alpha-naphthylamine and amido-naphthol disulphonate of soda—

$C_{20}H_{12}N_2S_2O_7Na_2 + 4H$
$$\doteq C_{10}H_7NH_2 + C_{10}H_4 . OH . NH_2 . (SO_3Na)_2$$

Alternative methods of standardising titanous chloride have been suggested by other workers.

Atack [1] has employed pure potassium chlorate for this purpose. The titanous chloride solution is made up and stored

---

[1] *J. S. D. and C.*, 1913, p. 9.

as described on p: 63. For standardising, about 50 c.c. of Methylene blue solution (4 grms. per litre) is run into a conical flask through which a current of carbon dioxide is maintained, heated to 40° and the solution just decolourised by running in titanous chloride. A solution containing a known weight of pure potassium chlorate (the amount of which must be less than what would be required to oxidise the whole of the leuco Methylene blue) is run in. This oxidises an amount of the leuco Methylene blue back to Methylene blue corresponding with the oxygen contained in the chlorate. The Methylene blue thus formed is titrated with titanous chloride in the ordinary way. The strength of the titanous chloride is thus ascertained and is expressed in terms of oxygen.

Paranitraniline has been advocated as a means of standard-ising titanous chloride for use in the estimation of nitro compounds by English [1] and by Callan and Henderson. [2] These authors find that whilst the original iron standard is a satisfactory one for inorganic determinations, the use of an organic nitro compound is to be preferred where organic compounds, especially nitro derivatives, are to be estimated. Moreover Callan and Henderson find that paranitraniline is a useful standard, because it may also be employed for standardising other solutions such as sodium nitrite, potassium bromate, aniline hydrochloride, etc.

For particular types of nitro compounds Callan and Henderson find that titanous sulphate may be used with advantage in place of titanous chloride, in fact they prefer it for all titrations. Whilst the concentration of the solution is of little importance they prefer to use in a works practice a solution of about 5 % strength in dilute sulphuric acid, so that correspondingly large amounts of nitro compound may be estimated. For the prepara-tion of such a solution, these authors mix 400 c.c. of commercial titanous sulphate with 500 c.c. dilute sulphuric acid (1 : 4), boil for a few minutes, cool and make up to 1 litre. The titanous sulphate made up as stated, is standardised by titrating (with the usual precautions) a known weight of pure paranitraniline (m.p. 149·5°). This determines the strength of the titanous sulphate, which in turn serves for the standardisation of the iron alum.

It is obvious that other substances might equally well find employment for standardising, provided that they are readily obtainable in a state of purity. The authors have, however,

[1] J. Ind. and Eng. Chem., 1920, p. 994.
[2] J. S. Chem. Ind., 1922, p. 158 T.

hitherto seen no advantage in deviating from the process of standardising as originally described.

Hendrixson and Verbeck [1] have recently described an electrometric method for the standardisation of titanous chloride, for details of which the original paper should be consulted. They mention that so intensely reducing is the titanous ion that an interval of nearly one volt is given between a slight excess of titanous ion and such oxidising agents as potassium bichromate and permanganate when the calomel-platinum cell is used, and this wide interval permits the determination of two oxidising agents of quite different intensities when present in the same solution.

ESTIMATION OF METALS

Estimation of Iron

Solutions containing the whole of the iron in the ferric condition may be titrated directly with the titanous chloride solution, using an excess of ammonium sulphocyanide as inside indicator. It is immaterial whether the iron is present in sulphuric or hydrochloric acid solution, but the presence of some mineral acid is essential, because the sulphocyanide indicator is otherwise not sensitive.

Methylene blue may also serve as indicator, but to obtain a rapid end point, the solution should be heated to about 35°.

If ferrous iron be present, this must first be oxidised to the ferric state, and then the estimation is carried out in the manner described. The method used for oxidising the ferrous iron to the ferric state may be chosen, according to circumstances, from one of the following :—

1. A known volume of the solution is treated with ammonia and hydrogen peroxide ; the excess of oxygen is driven off by boiling for from five to ten minutes, when excess of hydrochloric acid is added sufficient to dissolve the ferric hydrate.

2. To the sulphuric acid solution of ferrous salt add dilute potassium permanganate from a burette until the pink colour just becomes visible.

3. The ferrous solution is treated with a crystal of potassium chlorate and some hydrochloric acid. It is then boiled down to a small bulk, some water or dilute hydrochloric acid is added, the solution again evaporated down, and when the excess of chlorine has thus been removed the solution is ready for titration.

[1] *J. A. C. S.*, 1922, p. 2382.

Of these processes the first is most generally applicable. Hydrogen peroxide in alkaline solution is easily destroyed by boiling, and the ferric hydrate which is formed easily dissolves on acidifying the solution.

The use of potassium permanganate is only permissible in the absence of chlorides and in the presence of sulphuric acid.

In the third method the excess of oxidising agent takes a longer time to remove than does the hydrogen peroxide in alkaline solution.

Whichever process of oxidation is selected the subsequent method of estimating the iron is always the same.[1]

EXAMPLES.—1. *Estimation of ferrous and ferric iron in a sample of commercial copperas.*—1 grm. of copperas was dissolved in water and made up to 250 c.c. ; 50 c.c. was oxidised with hydrogen peroxide and ammonia as described and then titrated : required 22 c.c. TiCl$_3$.

$$1 \text{ c.c. TiCl}_3 = 0 \cdot 001823 \text{ grm. Fe}$$

∴ 50 c.c. solution contain $0 \cdot 001823 \times 22 = 0 \cdot 040106$ grm. Fe

that is, total iron = 20·05 %

2 grms. copperas dissolved in water, HCl and potassium sulphocyanide added : required 6·1 c.c. TiCl$_3$.

∴ 2 grms. copperas contain $0 \cdot 001823 \times 6 \cdot 1 = 0 \cdot 01112$ grms. Fe

that is, 0·556 % iron (ferric) or $\dfrac{0 \cdot 556 \times 160}{112} = \mathbf{0 \cdot 79} \%$ **Fe$_2$O$_3$**

The copperas contains, therefore—

$$(20 \cdot 05 - 0 \cdot 556) = 19 \cdot 494 \% \text{ iron (ferrous)}$$
$$\text{or } 19 \cdot 494 \times \tfrac{72}{56} = 25 \cdot 06 \% \text{ FeO}$$
$$\text{corresponding to } 96 \cdot 73 \% \text{ FeSO}_4 \cdot 7\text{H}_2\text{O}$$

2. *Ferrous and ferric iron in black liquor (ferrous acetate).*—50 c.c. was acidified with HCl and titrated : required 5·4 c.c. TiCl$_3$.

$$1 \text{ c.c. TiCl}_3 = 0 \cdot 001756 \text{ grm. Fe}$$

∴ 50 c.c. contain $0 \cdot 001756 \times 5 \cdot 4 = 0 \cdot 009482$ grm. Fe

that is, **0·1896** grm. Fe (ferric) per litre

10 c.c. was then made up to 100 c.c., and 10 c.c. of the diluted solution were evaporated to dryness and afterwards ignited, and the residue fused with bisulphate of potash. The product was then dissolved in water, acidified with hydrochloric acid, and titrated with titanous chloride, using potassium sulphocyanide as indicator. This required 31·9 c.c. TiCl$_3$.

10 c.c. of the diluted solution contain, therefore, $0 \cdot 001756 \times 31 \cdot 9 = 0 \cdot 05602$ grm. iron (ferrous and ferric), that is $(56 \cdot 01 - 0 \cdot 1896) = 55 \cdot 83$ grms. iron (ferrous) per litre.

3. *Estimation of ferrous and ferric iron in clay ironstone.*—2 grms. of a finely powdered sample of this ore were dissolved in HCl and the solution made up to 100 c.c.

[1] For a detailed account of the application of this method in the technical assay of iron ores and slags, see L. Brandt, *Chem. Ztg.*, 1924, p. 265 and 270.

10 c.c. was treated with ammonia and hydrogen peroxide, boiled, acidified and titrated with titanous chloride, using potassium sulphocyanide as indicator.

29·2 c.c. TiCl$_3$ was required (1 c.c. = 0·002012 grm. Fe).

∴ 10 c.c. or 0·2 grm. contain 0·05875 grm. Fe, and this equals 29·38 % iron (total).

2 grms. were dissolved and titrated without previously oxidising. This required 10·2 c.c. TiCl$_3$.

$$1 \text{ c.c. TiCl}_3 = 0·002012 \text{ grm. Fe}$$

∴ 2 grms. ore contain 0·002012 × 10·2 = 0·02052 grm. Fe

that is, **1·026** % iron (ferric)

The sample contains also 29·375 − 1·026 = **28·35** % iron (ferrous).

4. *Iron in iron wire.*—0·328 grm. iron wire was dissolved in hydrochloric acid, and the solution was made up to 250 c.c. 50 c.c. were treated with ammonia and hydrogen peroxide, boiled to expel excess of oxygen, then acidified and titrated with titanous chloride ; 40·55 c.c. TiCl$_3$ was required.

$$1 \text{ c.c. TiCl}_3 = 0·001613 \text{ grm. Fe}$$

∴ 50 c.c. contain 0·001613 × 40·55 = 0·065407 grm. Fe

that is, 0·32703 grm. Fe in 250 c.c. = **99·70** %

Estimation of Titanium

By reducing a titanic salt with zinc and hydrochloric acid in

FIG. 2.

a flask fitted with a Bunsen valve, the titanium is reduced to the condition of TiCl$_3$, and may be quantitatively estimated by titration with a standard solution of ferric iron, using sulphocyanide as indicator, or by titration with a standard solution of Methylene blue.

The simple apparatus used for carrying out the reduction of the titanic salt is shown in Fig. 2. It consists of a conical flask (capacity about 200 c.c.), into which the solution of the titanic salt is introduced along with some hydrochloric acid, and is fitted with a rubber stopper having three holes. One hole is fitted with a Bunsen valve, through which a platinum wire having a piece of zinc attached to it is passed, and the other two holes are temporarily closed with two glass rods. In this way the zinc is suspended in the titanium solution, and

when reduction has proceeded for 15 to 20 minutes one of the glass rods, A, is removed and a stream of carbon dioxide is passed into the flask, through a tube inserted in the same hole. The zinc is removed from the solution by raising the platinum wire through the small pierced indiarubber stopper at C, and the other glass rod, B, is then removed also. After the zinc has been washed with a little freshly boiled water from a wash-bottle, the solution is cooled and titrated with standard iron alum solution, using potassium sulphocyanide as indicator.

As an alternative the titanous solution may be titrated with standard Methylene blue, in which case it is best to heat the solution during the reduction process with zinc, and to titrate, while still warm, in a current of carbon dioxide.

EXAMPLE.—*Determination of titanous and titanic salt in a commercial titanous chloride solution.*

10·24 grms. was taken and diluted to 1 litre.

25 c.c. of the diluted solution of titanium was reduced with zinc and HCl as described and titrated with iron alum. Iron alum required = 20·3 c.c.

1 c.c. iron alum contains 0·00102 grm. Fe.

$$56 \; Fe = 48 \; Ti$$

$$\therefore \; 1 \text{ c.c. iron alum} = \frac{0 \cdot 00102 \times 48}{56} = 0 \cdot 0008742 \text{ grm. Ti}$$

25 c.c. of the solution contain 0·0008742 × 20·3 = 0·01775 grms. Ti. 25 c.c. of the diluted solution were titrated without reducing with zinc : required 19·6 c.c. iron alum.

that is, 0·0008742 × 19·6 = 0·01713 grm. Ti (titanous)

The titanium present as titanic salt is 0·01775 − 0·01713 = 0·0062 grm. ; therefore in the original solution there was present—

0·01713 × 40 = 0·685 grm. Ti (titanous)
in 10·24 grms. = 21·44 % TiCl$_3$
and 0·71 − 0·685 = 0·025 grm. Ti (titanic) = 0·96 % TiCl$_4$

Titanium and Iron in Admixture

Titanium may be estimated in the presence of iron by reduction with zinc and hydrochloric acid, and titration with either iron alum or Methylene blue, as previously described. The amount of iron present is estimated by titration with titanous chloride previous to reduction.

For the determination of titanium and iron in ores, the finely powdered substance is fused with about ten times its weight of caustic potash in a nickel dish. The melt is cooled, treated with water, reduced with zinc and hydrochloric acid in the apparatus

described under titanium and shown in Fig. 2, and then titrated with iron alum or Methylene blue.

The iron is estimated in the dissolved potash melt, after acidifying with hydrochloric acid, by direct titration with titanous chloride, using sulphocyanide as indicator.

EXAMPLES.—1. *Estimation of titanium and iron in rutile* (by the iron alum method).

0·4997 grm. of the ore was fused with potash, dissolved in HCl, and made up to 250 c.c.

25 c.c. of this solution was reduced with zinc and hydrochloric acid and titrated with iron alum.

<p style="text-align:center">Iron alum required = 17·3 c.c.</p>

1 c.c. iron alum contains—

$$0·001842 \text{ grm. Fe} = \frac{0·001842 \times 80}{56} = 0·002631 \text{ grm. TiO}_2$$

0·04997 grm. (25 c.c.) contains—

0·002631 × 17·3 = 0·04551 grm. = **91·07 %** TiO$_2$

1·96 grms. ore was fused with potash and dissolved in HCl as above, then titrated with titanous chloride : this required 26·1 c.c. TiCl$_3$.

1 c.c. TiCl$_3$ = 0·001432 grm. Fe = 0·002046 grm. Fe$_2$O$_3$

∴ 26·1 c.c. = 0·05340 grm. Fe$_2$O$_3$ = 2·72 % Fe$_2$O$_3$

2. *Estimation of titanium and iron in ilmenite* (Methylene blue method).

0·4055 grm. ilmenite fused with potash, dissolved in hydrochloric acid, and made up to 250 c.c.

50 c.c. was reduced with zinc and titrated with Methylene blue solution : required 31·8 c.c.

1 c.c. Methylene blue contains 0·001998 grm. colour.

319·5 Methylene blue solution = 160 grms. TiO$_2$

$$∴ 1 \text{ c.c. Methylene blue solution} = \frac{0·001998 \times 160}{319·5}$$
$$= 0·0010005 \text{ grm. TiO}_2$$

and 50 c.c. titanium solution contain—

0·0010005 × 31·8 = 0·031816 grm. TiO$_2$ = **39·21 %** TiO$_2$

50 c.c. of the same solution titrated with titanous chloride required 18·1 c.c.

1 c.c. TiCl$_3$ = 0·001542 grm. Fe = 0·002203 grm. Fe$_2$O$_3$

and 50 c.c. solution contain—

0·002203 × 18·1 = 0·039874 grm. Fe$_2$O$_3$

that is, 0·0811 grm. ore contain—

0·03987 grm. Fe$_2$O$_3$ = **49·16 %** Fe$_2$O$_3$

Copper

For the estimation of copper in copper sulphate about 1 grm. of the salt is dissolved in water and made up to 500 c.c.   50 c.c.

is measured into a conical flask, 10 c.c. standard iron alum solution added, and 10–20 c.c. of a 10 % solution of potassium sulphocyanide. The mixture is titrated with titanous chloride when the copper is first precipitated as white cuprous sulphocyanide, and then the red ferric sulphocyanide is reduced to the colourless ferrous salt, this remaining in solution. The amount of potassium sulphocyanide must be in excess, and as long as this is the case varying amounts of this reagent do not affect the result. The reaction is quantitative in the presence of varying amounts of hydrochloric and sulphuric acid, but nitric acid must not be present. The titration is best carried out at the ordinary temperature or below 30° C., and in an atmosphere of carbon dioxide.

EXAMPLE.—*Copper sulphate.*
A solution was made up containing 1 grm. in 500 c.c.

$$\text{and 50 c.c.} + \text{10 c.c. iron alum required 26·5 c.c. TiCl}_3$$
$$\text{10 c.c. iron alum required 9·8 c.c. TiCl}_3$$
$$\therefore \text{50 c.c. copper sulphate required 16·7 c.c. TiCl}_3$$
$$\text{1 c.c. TiCl}_3 = \text{0·001322 grm. Fe}$$
$$\text{249·5 grms. CuSO}_4 . \text{5H}_2\text{O} = \text{56 grms. Fe}$$

therefore 50 c.c. copper sulphate contain—

$$\frac{0·001322 \times 249·5 \times 16·7}{56} = 0·09833 \text{ grm.} = \mathbf{98·33} \text{ \%}$$

Copper and Iron in Admixture

EXAMPLE.—0·37 grm. of an ash containing *copper* and *iron* was fused with bisulphate of potash ; the fused mass was dissolved in water, made up to 100 c.c., and 25 c.c. titrated with titanous chloride.

$TiCl_3$ required = 31·0 c.c. (for copper and iron). Another 25 c.c. was taken, sulphuretted hydrogen was passed through the solution, the copper sulphide was filtered off, and the iron in the filtrate was oxidised by boiling with ammonia and hydrogen peroxide. The ferric hydrate was dissolved in HCl and titrated with $TiCl_3$.

$TiCl_3$ required = 16·1 c.c. (for iron) ; (31·0 − 16·1) = 14·9 c.c. $TiCl_3$ required for copper.

$$\text{1 c.c. TiCl}_3 = \text{0·002066 grm. Fe}$$
$$= \text{0·002951 grm. Fe}_2\text{O}_3$$
$$= \text{0·002914 grm. CuO}$$

$$\therefore \text{amount of Fe}_2\text{O}_3 \text{ present in ash} = \text{0·002951} \times \text{16·1} \times \text{4}$$
$$= \text{0·1900 grm. Fe}_2\text{O}_3$$
$$\text{and amount of CuO} = \text{0·002914} \times \text{14·9} \times \text{4}$$
$$= \text{0·1737 grm. CuO}$$

The ash contains therefore **51·35** Fe_2O_3 and **46·95** % CuO

Chromium

The following methods were suggested by S. B. Jatar [1] :—

1. Potassium bichromate is titrated with titanous chloride until a drop taken out gives no red colouration with a drop of a mixture of pure ferrous sulphate and potassium sulphocyanide solution.

2. Potassium bichromate is run into excess of pure ferrous sulphate, and the ferric iron which is formed is titrated in the usual way with titanous chloride.

The conversion of chromic salts into the condition of chromic acid may be effected by treating with ammonium persulphate in acid solution, and then boiling off the excess of oxygen. We prefer, however, to oxidise with sodium peroxide, boil off the excess of oxygen, and then neutralise the boiling solution by the addition of ammonium chloride. This process may be used with advantage for the valuation of chrome alum. It has also been found convenient to titrate the bichromate with excess of titanous chloride, add sulphocyanide, and then titrate back with iron. Whatever mode of procedure is adopted, it is necessary to avoid adding sulphocyanide until all the chromic acid is destroyed, because chromic acid acts upon sulphocyanide, producing persulphocyanogen.

The following example illustrates the method last described :—

EXAMPLE.—5 grms. of chromium acetate was dissolved in water and the solution made up to 100 c.c. Of this solution 10 c.c. was treated with sodium peroxide, boiled, the solution neutralised with ammonium chloride, and then titrated with titanous chloride in excess and the excess determined with iron alum.

$$TiCl_3 \text{ used} = 50 \text{ c.c.}$$

Excess by iron alum, 22·4 c.c. ; therefore 27·6 c.c. $TiCl_3$ was required by chromium.

$$1 \text{ c.c. } TiCl_3 = 0·001965 \text{ grm. Fe}$$
$$= \frac{0·001965 \times 100}{168} = 0·001169 \text{ grm. } CrO_3$$

$$0·001169 \times 27·6 = 0·0322644 \text{ grm. } CrO_3 \text{ in 10 c.c.}$$

∴ 50 grms. contain 3·226 grms. $CrO_3 = 6·44 \% CrO_3$
$$= 14·75 \% Cr(C_2H_3O_2)_3$$

[1] *J. S. C. I.*, 1908, p. 673.

Chromium and Iron in Admixture

The estimation of these metals, in the presence of each other, is best illustrated by an example of the analysis of a sample of chrome iron ore.

The method recommended by Jatar is as follows :—

0·5 grm. of the ore, which has been finely ground and passed through muslin, is fused with caustic soda or a mixture of caustic soda and sodium peroxide, with subsequent additions of the latter, in a silver dish over a Bunsen flame ; after fusing, the mass is extracted with water, the solution is boiled well to remove all traces of hydrogen peroxide, carefully acidified with dilute sulphuric acid, and again boiled.

In this way a mixture of ferric salt and chromic acid is obtained, and the solution may be made up to 500 c.c. and aliquot parts taken for titrations.

50 c.c. of the solution are titrated with titanous chloride, until all the chromic acid is destroyed, when potassium sulphocyanide is added, and the titration is continued until all the red colour due to ferric sulphocyanide is destroyed. This titration gives the total amount of chromium and iron.

The second titration, which gives the amount of iron alone, is based on the fact that hydrogen peroxide in acid solution reduces chromic acid to the chromic state, while ferric salts remain unchanged. 50–100 c.c. of the solution are taken, and hydrogen peroxide is added : the solution becomes purple owing to the formation of chromium peroxide, and afterwards green, showing that the bichromate is reduced to the chromic state. The amount of chromium is obtained by calculation from the difference between the two titrations.

We find that it is possible to estimate the iron alone by other methods. The most rapid method is to boil the melt with hydrochloric acid and a little alcohol, when the bichromate is reduced to chromic chloride. After cooling, the iron, which is not reduced by this treatment, may be titrated directly with titanous chloride.

EXAMPLE.—25 c.c. of a solution containing potassium bichromate and iron alum was found to require 30·4 c.c. $TiCl_3$ = amount required by chromium and iron. 25 c.c. of the solution was boiled with 5 c.c. hydrochloric acid and about 2 c.c. alcohol ; the solution was afterwards cooled and titrated as for iron. 25 c.c. treated in this way was found to require

$16 \cdot 2$ c.c. $TiCl_3$ = amount required by iron

$30 \cdot 4 - 16 \cdot 2 = 14 \cdot 2$ c.c. $TiCl_3$ = amount required by chromium

1 c.c. $TiCl_3 = 0 \cdot 001742$ grm. Fe

168 Fe = 52 Cr

1 c.c. $TiCl_3 = 0 \cdot 000539$ grm. Cr

$\therefore \ 0 \cdot 000539 \times 14 \cdot 2 = 0 \cdot 00765$ grm. Cr in 25 c.c. solution

and $0 \cdot 001742 \times 16 \cdot 2 = 0 \cdot 02822$ grm. Fe in 25 c.c. solution

The solution contains **0·306** grm. Cr per litre

and **1·129** ,,   Fe   ,,

As an alternative, the amount of titanous chloride necessary to reduce both chromium and iron is run into a measured portion of the solution, and the iron may then be titrated back with permanganate, or oxidised with chlorate and hydrochloric acid, which does not attack the chromic salt, but oxidises the iron to the ferric state ; the latter is titrated with titanous chloride. The last method is one which we have applied in estimating copper chromium and iron present in one solution.

In case iron and chromium are to be estimated in admixture, being present in the form of ferric and chromic oxides, the mode of procedure described in the following example has been found convenient :—

EXAMPLE.—$0 \cdot 228$ grm. ash from a piece of khaki cotton was fused with bisulphate of potash, and the fused mass was made up to 100 c.c. with water ; 25 c.c. of this solution was titrated with titanous chloride, using potassium sulphocyanide as indicator. $TiCl_3$ required $= 16 \cdot 4$ c.c. (for iron). 25 c.c. was oxidised with sodium peroxide as described under chromium. After expelling excess of oxygen, the solution was neutralised and titrated with titanous chloride. $TiCl_3$ required $27 \cdot 2$ c.c. (chromium and iron), so that $27 \cdot 2 - 16 \cdot 4 = 10 \cdot 8$ c.c. $TiCl_3$ required by chromium.

1 c.c. $TiCl_3 = 0 \cdot 001965$ grm. Fe

$= 0 \cdot 000889$,, Cr_2O_3

$= 0 \cdot 002807$,, Fe_2O_3

$0 \cdot 000889 \times 10 \cdot 8 \times 4 = 0 \cdot 03840$,, Cr_2O_3

$0 \cdot 002807 \times 16 \cdot 4 \times 4 = 0 \cdot 1841$,, Fe_2O_3

$Cr_2O_3 = $ **16·84** %

$Fe_2O_3 = $ **80·97** %

Copper and Chromium in Admixture

It is necessary in this estimation to have the copper present in the cupric condition, and the chromium as a salt of chromic acid. The amount of titanous chloride required to reduce both copper and chromium is first ascertained, and then alternative methods may be applied for determining one of the other

constituents. The simplest method is to pass SO_2 through the solution, and then, after boiling off excess, titrate the copper with titanous chloride as previously described. Another process, which is somewhat longer, is to first remove the copper with sulphuretted hydrogen, and then to oxidise the chromium to bichromate with hydrogen peroxide, when the bichromate is titrated with titanous chloride in the usual way.

If the copper and chromium are not present in the condition of cupric salt and chromic acid, it is necessary to oxidise and dissolve them. This is the case in determining copper and chromium in the ash of mordanted and dyed material. From 0·2 to 0·3 grm. of the ash is fused with bisulphate of potash ; the melt is dissolved in water and made up to a known volume. The copper is first titrated in one portion of the solution, and from another the copper is removed with sulphuretted hydrogen, and the chromium is oxidised with sodium peroxide ; the excess of oxidising agent is removed by boiling, and ammonium chloride is added. The solution is again boiled, then allowed to cool, and is titrated with titanous chloride.

EXAMPLE.—0·279 grm. mixed oxides fused with potassium bisulphate, and made up to 100 c.c. 25 c.c. titrated with $TiCl_3$ for copper estimation required 16·0 c.c.

From 25 c.c. the copper was removed with sulphuretted hydrogen. The chromium was oxidised with sodium peroxide and titrated with titanous chloride : required 26·0 c.c.

$$1 \text{ c.c. } TiCl_3 = 0·002001 \text{ grm. Fe}$$
$$= 0·002822 \text{ ,, } CuO$$
$$= 0·000905 \text{ ,, } Cr_2O_3$$

Therefore the ash contains—

0·002822 × 16 × 4 = 0·1806 grm. CuO = **64·73** %
0·000905 × 26 × 4 = 0·0945 ,, Cr_2O_3 = **83·9** %

Copper, Chromium, and Iron in Admixture

These metals are sometimes found together in the ash of mordanted and dyed material, and the following method has been used with success in estimating the mixed oxides. The mixture is fused with potassium bisulphate ; the melt is taken up with water and made up to a known volume. Portions of the solution are treated in the following way :—

1. Titrate with titanous chloride, using sulphocyanide as indicator. This gives the amount of iron and copper.

2. The copper is removed with sulphuretted hydrogen, and the iron, after oxidising with potassium chlorate, is determined

by titrating the filtrate with titanous chloride. This gives the amount of iron alone.

3. The copper is removed with sulphuretted hydrogen, and the chromium and iron are oxidised with sodium peroxide. The excess of oxygen is boiled off, hydrochloric acid is added, and the solution again titrated. By this means the total amount of chromium and iron is determined.

EXAMPLE.—The amounts of $TiCl_3$ used in titration were—
  (1) 19·7 c.c. required by iron and copper.
  (2) 8·8 c.c. required by iron.
  (3) 36·2 c.c. required by chromium and iron.
From these figures it will be seen that the copper present required 10·9 c.c., the chromium 27·4, and the iron 8·8 c.c. $TiCl_3$ (1 c.c. $TiCl_3$ = 0·002066 grm. Fe).

$$1 \text{ c.c. } TiCl_3 = 0·002951 \text{ grm. } Fe_2O_3$$
$$= 0·002914 \text{ ,, } CuO$$
$$= 0·000934 \text{ ,, } Cr_2O_3$$

The ash contained, therefore—

$$0·002951 \times 8·8 \times 4 = 0·1039 \text{ grm. } Fe_2O_3$$
$$0·002914 \times 10·9 \times 4 = 0·1270 \text{ ,, } CuO$$
$$0·000934 \times 27·4 \times 4 = 0·1027 \text{ ,, } Cr_2O_3$$

Estimation of Tin

One gram of the metal is dissolved in hydrochloric acid in presence of a small piece of platinum sponge, in a flask fitted with a Bunsen valve. Solution is accelerated by warming on a water-bath, but the temperature must never be allowed to rise sufficiently high to allow any vapour to escape. When the metal has completely dissolved, the solution is made up to 100 c.c., and 25 c.c. are run into a hot solution of iron alum of known strength, in an atmosphere of CO_2. When the solution has cooled, the excess of ferric iron is titrated with titanous chloride, using potassium sulphocyanide as indicator.

EXAMPLES.—25 c.c. tin solution prepared as described above was allowed to run into 50 c.c. iron alum solution.
(1 c.c. iron alum = 0·005628 grm. Fe.)
It was found that 35·7 c.c. $TiCl_3$ was required to reduce the excess of iron, and this amount corresponded to 7·9 c.c. iron alum.

∴ (50 − 7·9) = 42·1 c.c.
    = amount of iron alum required to oxidise $SnCl_2$
  112 Fe = 118 Sn

∴ 42·1 c.c. iron alum oxidise $\dfrac{0·005628 \times 118 \times 42·1}{112} = 0·2495$

and this is contained in 25 c.c. or 0·25 grm. tin = **99·80** %

In this estimation it is necessary to use a more concentrated solution of iron alum than is employed in other cases where titanous chloride is used in volumetric processes, in order that the amount of tin used for the experiment may be large. The method can also be used for estimating the reducing value of stannous chloride.

Stannous Chloride

Two grams stannous chloride are dissolved in hydrochloric acid and made up to 100 c.c. with water ; 25 c.c. are run into 50 c.c. of a warm solution of iron alum contained in a flask into which carbon dioxide is passed. The solution is allowed to cool, and then the excess of iron is titrated back with titanous chloride, using potassium sulphocyanide as indicator.

EXAMPLE.—25 c.c. of the *stannous chloride* dissolved as described above was added to 50 c.c. iron alum (1 c.c. = 0·005628 grm. Fe). The amount of titanous chloride required to titrate back was 27·0 c.c. $TiCl_3$ (4·35 c.c. $TiCl_3$ = 1 c.c. iron alum).

Therefore excess iron alum = 6·2 c.c.

$$\text{Iron alum used} = (50 - 6·2) = 43·8 \text{ c.c.}$$

$$\text{The amount of Sn present is } \frac{0·005628 \times 118 \times 43·8}{112} \text{ grms.}$$

$$= 0·2597 \text{ Sn} = 51·94 \% \text{ Sn}$$
$$\text{or } 99·04 \% \text{ SnCl}_2 . 2H_2O$$

Tungsten

In the reduction of tungstic acid with zinc and hydrochloric acid it is essential that the action should be vigorous, and for this reason strong hydrochloric acid must be employed. The colour of the solution almost immediately becomes dark blue, which after a short time becomes fainter and ultimately changes to a distinct brown, this marking the end of the reaction. If iron alum is now run into this solution without any sulphocyanide being present, the brown colour changes to blue, and by further additions this ultimately disappears, leaving a colourless liquid, which is rendered milky by the presence of white precipitated tungstic acid. The disappearance of the blue exactly coincides with the formation of the red when sulphocyanide is used as indicator. It is possible, therefore, to dispense altogether with the use of potassium sulphocyanide as indicator. It is important to note that the reduced solution should not be exposed to the air before or during titration.

EXAMPLE.—One gram of commercial *tungstate of soda* was dissolved in water and the solution made up to 100 c.c.

10 c.c. of this solution was reduced in a flask with a large excess of concentrated hydrochloric acid and pure granulated zinc until the brown colour was obtained. The reduced solution was titrated, while passing CO_2 through the flask, with iron alum until the blue colour disappeared. 17·1 c.c. iron alum was required.

$$1 \text{ c.c. iron alum} = 0\cdot001891 \text{ grm. Fe}$$
$$294 \text{ Na}_2\text{WO}_4 = 112 \text{ Fe}$$
$$\therefore 1 \text{ c.c. iron alum} = 0\cdot004963 \text{ grm. Na}_2\text{WO}_4$$

and 10 c.c. sodium tungstate solution contain—

$$0\cdot004963 \times 17\cdot1 = 0\cdot08486$$
$$= 84\cdot86 \text{ %}$$

Ferro-tungsten.—The alloy is ground in an agate mortar and sieved through calico. About 0·1 grm. is weighed in a porcelain crucible, and fused over a Bunsen with about 4 grms. of potassium persulphate until no more particles of metal are visible, which will require about 15 to 20 minutes. The melt is taken up in water, rendered alkaline with caustic soda, filtered from the ferric hydrate, and the tungsten estimated in the filtrate as described above. The iron can be estimated, if required, by dissolving the ferric hydrate in hydrochloric acid and titrating with titanous chloride, using sulphocyanide or Methylene blue as indicator.

Molybdenum

The titration of this metal is effected by means of a solution of Methylene blue (about 4 grms. per litre) which has been standardised by titration with titanous chloride.

EXAMPLE.—0·8 grm. of molybdic acid was dissolved in caustic soda and the solution made up to 100 c.c.

10 c.c. of this solution was transferred to a flask, and after adding a large excess of concentrated hydrochloric acid, the reduction was brought about by the addition of zinc. When the reduction was complete (which is indicated by the solution acquiring a salmon-pink colour), it was titrated with Methylene blue to the appearance of the blue colour. 25·55 c.c. Methylene blue was required.

$$1 \text{ c.c. Methylene blue} = 0\cdot002068 \text{ grm. Mo}$$

10 c.c. molybdic acid solution contain—

$$0\cdot002068 \times 25\cdot55 = 0\cdot05283 \text{ grm. Mo}$$
$$= 66\cdot04 \text{ % Mo}$$

Vanadium

The process described on p. 21 has been applied to the estimation of vanadium and chromium in a sample of steel.

EXAMPLE.—The steel drillings are fused with caustic soda and sodium peroxide. The melt is extracted with water, being digested on a water-bath for some time, filtered through toughened filter paper and the precipitate washed on the filter with hot water. The filtrate contains the whole of the chromium as chromate and the vanadium as vanadate and is made up to a known volume. An aliquot portion of this is run into a solution of leuco Methylene blue in excess and the regenerated Methylene blue is titrated with titanous chloride. This figure represents vanadium plus chromium. Another portion of the solution is acidified with sulphuric acid, filtered to remove silica (should any of this separate), reduced with sulphur dioxide and boiled for a short time. The solution is then oxidised by running in a solution of permanganate until a pink colour appears. This is coincident with the oxidation of the vanadium to the condition of V_2O_5 ; the chromic salt is not affected. The solution thus treated is added to leuco Methylene blue and the Methylene blue formed titrated with titanous chloride. The figure thus obtained represents the vanadium present.

The leuco Methylene blue solution required in these estimations is prepared as required by a very simple procedure. A stock solution of Methylene blue (medicinal, free from zinc) is prepared, containing about 4 grms. of the dyestuff per litre. 50 c.c. of this solution are run into a conical flask, acidified with hydrochloric acid and boiled. A current of carbon dioxide is then passed into the flask and dilute titanous chloride solution run in until the blue colour just disappears. It should be noted that all titrations in which leuco Methylene blue is used should be done in an atmosphere of carbon dioxide.

The following results were obtained on a sample of tool steel :—

	I.	II.	III.
Vanadium % . . .	0·538	0·540	0·537
Chromium % . . .	1·17	1·18	1·18

The author of the method states that the presence of tungsten or molybdenum would vitiate the result.

NON-METALLIC ELEMENTS AND THEIR COMPOUNDS

Hydrogen Peroxide

For the analysis of a commercial sample 10 c.c. was diluted with distilled water to 250 c.c. Of this solution, 10 c.c. was titrated with titanous chloride. At first an intense orange-yellow colour appears ; this attains a maximum intensity, and gradually fades to colourless as the titration proceeds. The latter point marks the end of the reaction.

EXAMPLE.—10 c.c. hydrogen peroxide (made up as above) required 18·3 c.c. TiCl₃.

$$1 \text{ c.c. TiCl}_3 = 0\text{·}002301 \text{ grm. Fe}$$
$$56 \text{ Fe} = 17 \text{ H}_2\text{O}_2 = 8 \text{ O}$$
$$\therefore 1 \text{ c.c. TiCl}_3 = \frac{0\text{·}002301 \times 8}{56} = 0\text{·}0003287 \text{ oxygen}$$

10 c.c. diluted H_2O_2 correspond, therefore, to—

$$0\text{·}0003287 \times 18\text{·}3 = 0\text{·}006015 \text{ oxygen}$$

and 250 c.c. contain—

0·006015 × 25 = 0·1504 grm. oxygen

1 grm. oxygen = 697·5 c.c. at 0° C. and 760 mm. pressure

that is, 10 c.c. of the sample evolve 104·9 c.c. oxygen.

Hydrogen peroxide = **10·49** volumes or **3·19** %

Perborates

Perborates can be estimated by the method given for hydrogen peroxide. As an alternative, a known weight of the perborate may be added to an acidulated solution of ferrous ammonium sulphate, and the ferric salt formed titrated with titanous chloride.

EXAMPLE.—0·118 grm. sodium perborate was added to about 2 grms. ferrous ammonium sulphate dissolved in water and acidulated with sulphuric acid. Potassium sulphocyanide was added, and the solution titrated with titanous chloride, of which 38 c.c. was required.

1 c.c. Ti Cl₃ = 0·000323 grm. oxygen

38 × 0·000323 = 0·01227 grm. oxygen in 0·118 grm. sample

This gives **10·39** % available oxygen.

For the estimation of the available oxygen in washing powders, Moser and Seeling [1] have compared different methods and come to the conclusion that the titration with titanous chloride is specially suited for the purpose.

[1] *Z. f. Anal. Chem.* 1913, p. 73.

EXAMPLE.—4·2892 grms. of a washing powder was dissolved in cold water, and 40 c.c. dilute sulphuric acid added. The solution was added to a flask containing excess of titanous chloride through which a current of CO_2 was maintained. The excess of titanous chloride was ascertained by back-titration with iron alum.

18·9 c.c. $TiCl_3$ used up.

1 c.c. $TiCl_3$ = 0·004934 grm. Fe,
corresponding to 0·311 % available oxygen.

Persulphates

These are estimated indirectly. About 1 grm. of the sample is dissolved in cold water and the solution made up to 100 c.c. To 10 c.c. of this solution a known volume of titanous chloride is added, the amount being in excess of that required to reduce the persulphate. The excess of titanous chloride is estimated by titrating back with iron alum.

EXAMPLE.—1·02 grm. *ammonium persulphate* was dissolved in water and the solution made up to 100 c.c. To 10 c.c. of this solution 50 c.c. $TiCl_3$ (1 c.c. = 0·002031 grm. Fe) was added. By titrating back with iron alum the excess of $TiCl_3$ was found to be 28·0 c.c., so that 22 c.c. had been used up by the reduction of the persulphate.

$$114 \ NH_4SO_4 = 56 \ Fe$$

∴ 0·102 grm. NH_4SO_4 contain—

$$\frac{0·002031 \times 114 \times 22}{56} = 0·090948 = 88·14 \ \%$$

Chlorates

These salts are best estimated by introducing a known quantity into an excess of titanous chloride, and titrating back the excess with iron alum, using sulphocyanide as indicator.

EXAMPLE.—*Sodium chlorate.* 0·95 grm. sodium chlorate dissolved in water and made up to 500 c.c.

50 c.c. standard titanous chloride (1 c.c. = 0·0015 grm. Fe) is run into 5 c.c. concentrated hydrochloric acid contained in a conical flask through which a current of carbon dioxide is maintained. 10 c.c. of the sodium chlorate solution are added. After a lapse of not less than three minutes potassium sulphocyanide is added, and the excess of titanous chloride is estimated by titration with standard iron alum solution, until a permanent red colour is obtained. All the values are based upon an iron standard, and six equivalents of iron are equal to one molecule of chlorate.

$$106·5 \ NaClO_3 = 336 \ Fe$$

1 c.c. $TiCl_3$ = 0·001513 grm. Fe = $\dfrac{0·001513 \times 106·5}{336}$

$$= 0·0004796 \ grm. \ NaClO_3$$

10 c.c. sodium chlorate contain—

$$0.0004796 \times 37.5 = 0.01798 \text{ grm. } NaClO_3$$

that is, 0.95 contains 0.899 ;

$$\therefore \text{ sodium chlorate} = \mathbf{94.63} \text{ \%}$$

EXAMPLE.—*Chlorate in bleaching powder.*

The available chlorine was first determined by adding potassium iodide and starch, and titrating with thiosulphate of soda in the presence of acetic acid. This was found to be 31.8 %.

The total chlorine due to hypochlorite and chlorate was estimated in the following way : 10 grms. bleaching powder was made up to 1 litre, and 10 c.c. was titrated with excess of titanous chloride (50 c.c.) in an atmosphere of carbon dioxide, and then titrated back with iron alum.

Iron alum required $= 20.2$ c.c.

The hypochlorite and chlorate required $50 - 20.2 = 29.8$

1 c.c. $TiCl_3 = 0.001162$ grm. Cl

$\therefore$ hypochlorite and chlorate $= 0.001162 \times 29.8 = 0.03463$ grm. Cl

hypochlorite $= 0.03180$ grm.

Therefore the chlorate present corresponds to

$$0.03463 - 0.03180 = 0.00283 \text{ grm. Cl}$$
$$= \mathbf{2.83} \text{ \% Cl present as chlorate}$$

Perchlorates

The estimation of these substances depends upon their complete reduction in concentrated and strongly acid solution. The reduction does not take place in dilute solution. Potassium perchlorate is best dissolved in a strong solution of oxalic acid.

The mode of procedure is best illustrated by the following example :—

EXAMPLE.—Dissolved 0.1125 grm. potassium perchlorate in 10 c.c. of a saturated solution of oxalic acid, added 10 c.c. concentrated sulphuric acid and 10 c.c. strong titanous chloride (20 %) ; allowed to stand for about five minutes, then cooled and made up to 100 c.c.

10 c.c. of this solution was titrated with iron alum.

A blank was made with 10 c.c. saturated oxalic acid solution, 10 c.c. concentrated sulphuric acid, 15 c.c. titanous chloride, made up to 100 c.c., and 10 c.c. of this was titrated with iron alum.

Iron alum required before adding $KClO_4$ $= 34.8$ c.c.

„ „ „ after „ „ $= 21.7$ „

„ „ equivalent of $TiCl_3$ used by $KClO_4 = 13.1$ „

1 c.c. iron alum $= 0.002763$ grm. Fe

138.5 grm. $KClO_4 = 448$ Fe

$$13.1 \text{ c.c. iron alum} = \frac{0.002763 \times 13.1 \times 138.5}{448}$$
$$= 0.011182 \text{ grm. in } 0.1125 \text{ grm.}$$
$$= \mathbf{99.38} \text{ \%}$$

Nitrates

Three reduction methods are available for the estimation of nitrates.

Method I.—This is really a modification of the Pelouze process, and may be carried out in the following way :—

About 1 grm. of the nitrate is dissolved in water and made up to 500 c.c.

About 2 grms. pure ferrous sulphate are dissolved in the smallest possible volume of water and 10 c.c. concentrated hydrochloric acid are added. To this there is added 10 c.c. of the nitrate solution. The mixture is boiled in a flask through which carbon dioxide is passed ; then allowed to cool and titrated with titanous chloride solution, which estimates the amount of ferric iron produced.

EXAMPLE.—0·996 grm. sodium nitrate was dissolved in 500 c.c.
10 c.c. was allowed to act on ferrous sulphate as above, and the ferric iron titrated with titanous chloride.

$$1 \text{ c.c. TiCl}_3 = 0 \cdot 001735 \text{ grm. Fe}$$
$$63 \text{ HNO}_3 \text{ or } 85 \text{ NaNO}_3 = 168 \text{ Fe}$$

The solution required 22·1 c.c. $TiCl_3$.

$$1 \text{ c.c. TiCl}_3 = \frac{0 \cdot 001735 \times 85}{168} = 0 \cdot 0008777 \text{ grm. NaNO}_3$$

10 c.c. contained—

$$0 \cdot 0008777 \times 22 \cdot 1 = 0 \cdot 019397 \text{ grm. NaNO}_3 = \mathbf{97 \cdot 8 \%}$$

Method II.—This depends upon the nitration of phenol and the estimation of the picric acid formed with titanous chloride.

For this purpose 3 grms. phenol is heated on a water-bath with 20 c.c. conc. sulphuric acid for six hours, and the nitrate to be estimated is heated for an hour on the water-bath with 5 c.c. of this solution. The amount of nitrate taken should correspond to from 0·005 to 0·02 grm. KNO_3. The nitro compound is then dissolved in water and titrated with titanous chloride (see Nitro compounds). The mode of procedure is shown in the following example of the estimation of nitrate in water.

EXAMPLE.—*Nitrates in water.* 100 c.c. of the water is evaporated in a porcelain dish, and the residue is treated with 5 c.c. phenol sulphonic acid.

The nitro compound was dissolved in water, hydrochloric acid was added, and the solution reduced with a large excess of titanous chloride (50 c.c.). When this had been cooled, the excess of titanous

chloride was titrated back with iron alum, using potassium sulpho-cyanide as indicator.

$$\text{Iron alum required} = 35 \cdot 8$$
$$\therefore \text{TiCl}_3 \text{ used in reduction} = 50 - 35 \cdot 8 = 14 \cdot 2 \text{ c.c.}$$
$$\text{1 c.c. TiCl}_3 = 0 \cdot 001612 \text{ grm. Fe}$$
$$63 \text{ HNO}_3 = 336 \text{ Fe}$$
$$\text{and 1 c.c. TiCl}_3 = \frac{0 \cdot 001612 \times 63}{336} = 0 \cdot 0003022 \text{ grm. HNO}_3$$

100 c.c. water contain $0 \cdot 0003022 \times 14 \cdot 2 = 0 \cdot 00429$ grm. HNO_3

that is, nitrates corresponding to $4 \cdot 29$ grms. HNO_3 in 100,000 c.c. water.

Method III.—A convenient amount of nitrate for a single estimation is about the equivalent of $0 \cdot 1$ grm. potassium nitrate. In the assay of a commercial sodium nitrate, about 1 grm. is accurately weighed, dissolved in water, and made up to 100 c.c. Of this 10 c.c. are measured into a copper flask, excess of caustic soda is added, and then about 20 c.c. of commercial titanous sulphate or chloride whilst the contents of the flask are kept in motion by swirling. The distillation can then at once be proceeded with, and, after the boiling has been continued for a quarter of an hour, the operation is finished, and back titration is effected.

It is essential that the reagents should be added in the sequence as stated, for if the acid solution of the titanous salt is allowed to react with the nitrate, reactions take place which result in the expulsion of a portion of the nitrogen, either as nitrous or nitric oxide, and the result is consequently unreliable. It is also obvious that the titanous salt should be free from ammonia.

Two estimations, carried out in the manner described, on pure potassium nitrate gave respectively $99 \cdot 80$ and $99 \cdot 83$ %.

Method IV.—Reduction to ammonia by $TiCl_3$ and NaOH and titration of the distillate with N/10 sulphuric acid (see p. 26).

Hydroxylamine

A known amount (about 1 grm.) of the hydroxylamine salt is dissolved in boiling water, and made up to 100 c.c. An aliquot part of this solution is titrated with excess of titanous chloride is an atmosphere of CO_2.

The excess of titanous chloride is estimated by titrating back with potassium permanganate solution.

EXAMPLE.—1 grm. hydroxylamine hydrochloride, $NH_3O . HCl$, was dissolved in 100 c.c. water, and 10 c.c. was titrated with 50 c.c. $TiCl_3$.

Excess $TiCl_3$ by titrating with permanganate [1] = 5·9 c.c. The hydroxylamine required, therefore, 44·1 c.c. $TiCl_3$.

69·5 grms. hydroxylamine hydrochloride = 112 Fe

1 c.c. $TiCl_3$ = 0·00354 grm. Fe

$$\therefore \quad 1 \text{ c.c. } TiCl_3 = \frac{0 \cdot 00354 \times 69 \cdot 5}{112} = 0 \cdot 002196 \text{ grm.}$$

0·1 grm. hydroxylamine solution contains—

0·002196 × 44·1 = 0·09684 grm. = **96·84** %

Oxygen in Water

The following solutions are required for this estimation :

10 % solution ferrous sulphate containing a little sulphuric acid and a small coil of iron wire ; 20 % solution of caustic soda ; concentrated hydrochloric acid ; potassium sulphocyanide ; and titanous chloride in the storage burette.

Into a flask through which carbon dioxide is passing 100 c.c. of the water to be examined, 5 c.c. ferrous sulphate solution, and 1 c.c. caustic soda are introduced. The contents are allowed to stand about three minutes, when 1·5 c.c. HCl are added, and 1 c.c. potassium sulphocyanide. The ferric iron is then estimated with titanous chloride.

It is necessary to use small volumes of the reagents, and the capacity of the flask should be not more than 100 c.c.

EXAMPLE.—A sample of water was treated in the manner described above, and the ferric iron produced was found to require 14·2 c.c. $TiCl_3$.

1 c.c. $TiCl_3$ = 0·0004414 grm. Fe = 0·00006306 grm. O

100 c.c. of the water contain therefore—

0·00006306 × 14·3 = 0·00090176 grm. O
= 6·26 c.c. oxygen per litre

Hydrosulphites

A known weight of the sample is allowed to reduce a solution of Methylene blue. The latter must be present in excess, and this is estimated by subsequent titration with titanous chloride.

For this purpose a standardised solution of Methylene blue containing about 14 grms. per litre is required. 50 c.c. of this

[1] In place of permanganate, iron alum can be used for this titration.

solution is measured into a conical flask, through which a current of carbon dioxide is maintained.

0·1 to 0·2 grm. hydrosulphite is introduced from a weighing bottle, 10 c.c. acetic acid is added ; the solution is heated and titrated with titanous chloride.

In order to ascertain how much titanous chloride is required by 50 c.c. Methylene blue solution, this is titrated in the same way, without the introduction of hydrosulphite.

The difference between the number of c.c. $TiCl_3$ required in these two titrations gives the amount equivalent to the hydrosulphite used.

EXAMPLE.—0·1995 grm. *sodium hydrosulphite* was introduced into 50 c.c. Methylene blue, and the solution titrated as described above required 24·4 c.c. $TiCl_3$.

50 c.c. Methylene blue require alone 76·26 c.c. $TiCl_3$.

∴ 76·26 − 24·4 = 51·86 c.c. $TiCl_3$ = 0·1995 grm. hydrosulphite

1 c.c. $TiCl_3$ = 0·002001 grm. Fe

112 Fe = 319·5 Methylene blue = 174 $Na_2S_2O_4$

∴ 1 c.c. $TiCl_3 = \dfrac{0 \cdot 002001 \times 174}{112} = 0 \cdot 003108\ Na_2S_2O_4$

58·86 c.c. $TiCl_3$ = 0·003108 × 51·86 = 0·16118 grm. $Na_2S_2O_4$

corresponding to **80·79** %

Sodium sulphoxylate-formaldehyde (hyraldite, rongalite, hydrosulphite NF).

Sodium sulphoxylate in hydrosulphite NF conc. may be estimated by titanous chloride in a similar way.

EXAMPLE.—A solution of 1·075 grm. in 100 c.c. hydrosulphite NF was employed. 25 c.c. Methylene blue solution (10 grm. per litre) was placed in a conical flask, carbon dioxide was passed in, 10 c.c. acetic acid, and 10 c.c. hydrosulphite NF solution added. The mixture was then allowed to stand five minutes, boiled fifteen minutes, passing the current of CO_2 into the flask all the time, and then titrated with titanous chloride until the blue colour of the excess Methylene blue was removed.

The hydrosulphite NF reduces its equivalent of Methylene blue, which is expressed in terms of titanous chloride.

25 c.c. Methylene blue required alone 38·13 c.c. $TiCl_3$,

25 c.c. Methylene blue with 10 c.c. hydrosulphite NF required 9·23 c.c. $TiCl_3$;

∴ (38·13 − 9·23) = 28·9 c.c. $TiCl_3$ equivalent to hydrosulphite

1 c.c. $TiCl_3$ = 0·0023 grm. Fe $= \dfrac{0 \cdot 0023 \times 88}{112}$

= 0·0018 grm. $NaHSO_2$

∴ 10 c.c. or 0·1075 grm. hydrosulphite NF contain 0·0018 × 28·9

= 0·05202

Sodium sulphoxylate = **48·38** %

An alternative mode of procedure in valuing a commercial solid hydrosulphite is to add from a weighing bottle a suitable quantity of the hydrosulphite (0·1–0·2 grm.) to a flask containing 20 c.c. of approximately decinormal bichromate which has been previously rendered alkaline by means of caustic soda. The alkali should be in excess of that required to convert the bichromate into chromate. The contents of the flask are then boiled for four to five minutes, after which the chromium hydrate is filtered through an ordinary filter, washed, and transferred along with the filter to a beaker in which the chromium hydrate is converted into chromate by boiling with water to which a small quantity of sodium peroxide is added. The boiling is continued until the whole of the sodium peroxide is decomposed, when the filtered solution is acidulated with sulphuric acid, and the chromium estimated by adding excess of titanous chloride and titrating back with iron alum.

The following figures give the results obtained in a typical case :—

Methylene blue method	.	.	.	.	89·2 % $Na_2S_2O_4$
Sinnatt's method	.	.	.	.	.	88·8 ,, ,,
Chromate method	.	.	.	.	.	89·1 ,, ,,

The chromate method is not affected by the presence of bisulphites. Thus the sample quoted above yielded in presence of such a large excess as 10 c.c. sodium bisulphite (18 % SO_2) 89 % $Na_2S_2O_4$. Similarly, the presence of thiosulphates was found to be without influence on the accuracy of the estimation.

The filtrate from the chromium hydrate contains all the sulphite formed by the oxidation of the hydrosulphite, and the sulphite from any bisulphite which might have been present in the sample. If, therefore, excess of an accurately measured quantity of $\frac{N}{10}$ bichromate is taken in the estimation, it is possible, after having estimated the hydrosulphite, to carry the oxidation as far as to sulphate (or sulphuric acid) by acidulating the filtrate—

$$2CrO_3 + 3SO_2 + 3H_2O = Cr_2O_3 + 3H_2SO_4$$

and then the excess of chromate is determined by titration. By subtracting the sulphite formed by the hydrosulphite from the total sulphite, the sulphite present in the sample as such or as bisulphite is obtained.

In order to overcome the necessity of using very small quantities of sodium hydrosulphite for an estimation Crowther and Heywood [1] convert larger samples (about 12 grms.) into

[1] *J. S. D. and C.*, 1920, p. 280.

the formaldehyde compound and thus ensure better sampling. The solution of the formaldehyde compound is made up to a litre and is run from a burette into a known amount of Methylene blue solution in dilute acetic acid, which has previously been standardised with titanous chloride. The estimation is carried out in the following way :—40 c.c. 40 % formaldehyde solution are added to 800 c.c. air-free water in a graduated litre flask ; after adding 10 c.c. 30 % caustic soda, the contents of the flask are swirled vigorously and about 8–12 grms. of hydrosulphite powder, contained in a weighed stoppered weighing bottle, is dribbled in through a dry funnel the stem of which is of sufficient length to ensure that no powder impinges upon any part of the flask. The rate of addition may be fairly rapid as the powder is readily dissolved while falling through the swirling liquid. A cake of undissolved material at the bottom of the flask indicates a too rapid addition of the powder and leads to somewhat low results. Any of the powder adhering to the funnel is washed in with 10 c.c. formaldehyde solution, followed by a little water, and the contents of the flask are adjusted to the mark. A second weighing of the weighing bottle gives the exact weight of powder taken. 25 c.c. standard Methylene blue solution are measured into an Erlenmeyer flask of 200 c.c. capacity, 10 c.c. glacial acetic acid and 50 c.c. water are added. A stream of carbon dioxide is passed over and the solution is heated to the boil. The formaldehyde hydrosulphite solution is then run in from a burette. The end of the reaction is indicated by a sharp change through blueish-green to yellow. As an alternative process a known volume of the hydrosulphite formaldehyde may be added to excess of Methylene blue, which is estimated with titanous chloride.

For determining the amount of hydrosulphite present in an indigo vat A. Lauterbach [1] has found the titanous chloride method with Methylene blue to be satisfactory, but to obtain a more rapid end point in titrating with titanous chloride he recommends the addition of a small quantity of salicylic acid to the solution of Methylene blue. The method of carrying out the test on a vat is as follows :—

5 c.c. of a 50 % zinc sulphate solution (containing 0·2 c.c. of acetic acid 10° Tw.) are run into a 100-c.c. measuring flask and carbon dioxide is passed in by means of a tube which does not dip below the surface of the liquid. When the air has been displaced, a small quantity of bicarbonate of soda is added. The

[1] *Rep. 7th Congr. Internat. Verg. d. Chem.-Kol.*, 1922, pp. 33–47.

formaldehyde solution is then prepared in a beaker by adding about a gram of ammonium carbonate to about 80 c.c. formaldehyde. 20 c.c. of the vat liquor are then run into the flask, care being taken to place the delivery end of the pipette near the surface of the liquid. The stopper with the carbon dioxide tube is replaced and the contents of the flask are swirled round. Then formaldehyde solution is added, the flask again swirled, and the contents are now filled up to the mark with water, the flask being closed by inserting the stopper. After standing five minutes it can be filtered.

In case no suspended indigo is present, the precipitate which forms before the addition of the formaldehyde should be pure white. After the addition of the latter, it becomes yellow and then usually a bright orange. The liquor has then a light yellow colour and shows a faint green fluorescence. If it shows a green colour or a strong green fluorescence this indicates that insufficient ammonium carbonate has been added to the formaldehyde.

Methylene blue solution (excess) of known strength is now run into the titration flask and 5 c.c. acetic acid (10° Tw.) is added. While passing carbon dioxide through the flask a little carbonate of soda is added and the temperature brought to 90° ; 50 c.c. of the precipitated and filtered vat liquor is now run in and the heating is continued until the temperature reaches 94°. The flame is then removed and 40 c.c. acetic acid (10° Tw), containing 0·5 c.c. HCl, along with a little sodium bicarbonate to sweep out dissolved oxygen, is added, then 0·15 grm. salicylic acid. The excess of Methylene blue is now titrated with titanous chloride. The author maintains that an estimation can be done in twenty minutes. The method can be used to test hydrosulphite vats of other vat colours from which the leuco colour can be removed like indigo.

Sulphites and Bisulphites

EXAMPLE.—*Estimation of total SO_2 in a sample of commercial bisulphite of soda.*

10 c.c. of the sample are diluted to 100 c.c. Of this solution 10 c.c. is run into a solution of 20 c.c. $\dfrac{N}{10}$ bichromate of potash which had been previously rendered alkaline by the addition of caustic soda in excess. It is then acidified by gradually adding dilute sulphuric acid, when the oxidation of sulphite to sulphate at the expense of the chromic acid is quantitative. The titration of the excess of chromic acid is then effected by means of standard

solutions of titanous chloride and of iron alum.   20 c.c. bichromate solution (containing 0·09872 grm.) + 10 c.c. bisulphite required 40·9 c.c. $TiCl_3$.

$$1 \text{ c.c. } TiCl_3 = 0·001763 \text{ grm. } K_2Cr_2O_7$$
$$40·9 \text{ c.c. } TiCl_3 = 0·072107 \text{ grm. } K_2Cr_2O_7$$

Therefore 10 c.c. bisulphite reduce

$$0·09872 - 0·072107 = 0·02661 \text{ grm. } K_2Cr_2O_7$$

and since $K_2Cr_2O_7(294) = 3SO_2(192)$

∴   0·02661 $K_2Cr_2O_7 = 0·01738$ grm. SO_2

The full strength solution contains 17·38 grms. SO_2 per 100 c.c.

The same sample, by the method of Giles and Shearer, gave 17·31 grms. SO_2 per 100 c.c.

This method, while being rapid and exact, is free from the uncertainties which attach (according to some authorities) to the iodine method.

ORGANIC COMPOUNDS

Nitro Compounds

The indirect method (III.) described for the estimation of azo dyes (see p. 29) is applicable also to all nitro compounds which are soluble in water. Care must be taken, however, to use a large excess of titanous chloride, and to boil for about ten minutes with the reducing agent. By observing these precautions the reduction is complete, six equivalents of titanous chloride being required for the reduction of each nitro group.

EXAMPLE.—*Picric acid,* $C_6H_2(OH)(NO_2)_3$.

1 grm. of picric acid was dissolved in 1 litre of water.   10 c.c. of this solution was acidified with HCl, and 50 c.c. titanous chloride was added ; boiled for ten minutes, and then cooled.

24·1 c.c. iron alum were required to titrate excess $TiCl_3$.

$$24·1 \text{ c.c. iron alum} = 26·6 \text{ c.c. } TiCl_3 = \text{excess used}$$

∴   0·01 grm. picric acid required for reduction 23·4 c.c. $TiCl_3$

$$229 \text{ picric acid} = 1008 \text{ Fe}$$
$$1 \text{ c.c. } TiCl_3 = 0·001854 \text{ grm. Fe}$$

This amount of the sample contains therefore—

$$\frac{0·001854 \times 229 \times 23·4}{1008} = 0·009856 \text{ grm.}$$

$$= \mathbf{98·56 \%}$$

The entire estimation is conducted in a current of carbon dioxide, and this applies to all estimations carried out by the indirect method.

Naphthalene in Coal Gas.[1]—The method depends upon the formation of naphthalene picrate and the estimation of the picric acid by means of titanous chloride, and only differs from the process described for the estimation of picric acid in that the naphthalene picrate is dissolved in alcohol.

Naphthalene picrate is separated by any of the usual processes, and about 20 c.c. alcohol and 20 c.c. concentrated hydrochloric acid are added. The solution is boiled, excess of titanous chloride is added, and after cooling, the excess of titanous chloride is estimated by means of iron alum, using potassium sulphocyanide as indicator.

EXAMPLE.—Naphthalene picrate, obtained by passing a litre of coal gas through a solution of picric acid, was dissolved in alcohol and reduced as described above with 50 c.c. $TiCl_3$

$$\text{Excess } TiCl_3 = 30 \text{ c.c. (by iron alum)}$$
$$\text{titanous chloride used by picric} = 20 \text{ c.c.}$$
$$1 \text{ c.c. } TiCl_3 = 0\cdot001784 \text{ grm. Fe}$$
$$1008 \text{ Fe} = 229 \text{ picric} = 126\cdot98 \text{ naphthalene}$$
$$\therefore 1 \text{ c.c. } TiCl_3 = 0\cdot0002248 \text{ grm. naphthalene}$$
$$\text{The amount present} = 0\cdot004496 \text{ grm. naphthalene per litre}$$

Aryl-guanidines.—Callan[2] has successfully employed a method of valuing these substances (which are extensively used as accelerators in the vulcanisation of rubber), by converting the commercial product into the picrate and then estimating the amount of picric acid contained in a known weight of the latter by titration with titanous sulphate.

EXAMPLE.—0·4004 grm. of a sample of commercial triphenyl-guanidine $C_6H_5N : C(NC_6H_5)_2$ thus treated gave 0·7114 grm. picrate. A known weight (about 0·1 grm.) of this was dissolved in concentrated sulphuric acid, the solution made up to 250 c.c. and an aliquot portion titrated in the manner indicated for picric acid. This gave 98·8 % calculated as triphenyl guanidine. The m.p. was 179·5–181° (pure gives 181–181·5°) and the M.W. calculated from the analysis of the picrate was 290 (theoret. 287).

Naphthol yellow S, $C_{10}H_4(NO_2)_2$. ONa . SO$_3$Na (di-sodium salt).

The process has also proved valuable for the estimation of Naphthol yellow S, which requires twelve equivalents of titanous chloride.

This estimation is conducted in exactly the same way as described for picric acid. An estimation of the disodium salt may serve as an example.

[1] F. S. Sinnatt, *Proc. Chem. Soc.*, 1905, p. 297.
[2] *J. S. C. I.*, 1924, p. 1.

EXAMPLE.—0·25 grm. *Naphthol yellow* was dissolved in 250 c.c. water.

25 c.c. solution required (50 c.c. $TiCl_3$ used ; 27·6 c.c. excess by iron alum) = 22·4 c.c. $TiCl_3$.

$$1 \text{ c.c. } TiCl_3 = 0\text{·}001792 \text{ grm. Fe}$$

358 Naphthol yellow require 672 iron ; therefore 25 c.c. solution contain—

$$\frac{0\text{·}001792 \times 358 \times 22\text{·}4}{672} = 0\text{·}02138 \text{ grm. Naphthol yellow S}$$

$$= 85\text{·}53 \%$$

Paranitraniline is estimated in the same way as picric acid, but is first dissolved in hydrochloric acid.

EXAMPLE.—1·013 grm. *p-nitraniline* was dissolved in hydrochloric acid and made up to 1 litre with water. 25 c.c. of this solution was reduced with 50 c.c. $TiCl_3$ in the usual way, and then titrated back with iron alum. Excess $TiCl_3 = 17\text{·}28$ c.c.

The *p*-nitraniline uses, therefore, 32·72 c.c. $TiCl_3$.

$$1 \text{ c.c. } TiCl_3 = 0\text{·}001854 \text{ grm. Fe}$$
138 *p*-nitraniline, $C_6H_4NO_2 . NH_2 = 336$ Fe

therefore 0·02532 grm. contains—

$$\frac{0\text{·}001854 \times 138 \times 32\text{·}72}{336} = 0\text{·}02491 \text{ grm.}$$

$$= 98\text{·}36 \%$$

Compounds like nitrobenzene and nitrotoluene are most conveniently titrated in the sulphonated condition.

EXAMPLE.—*Nitrobenzene,* $C_6H_5 . NO_2$.

1·002 grms. was sulphonated by heating with 20 c.c. fuming sulphuric acid on a water-bath for two hours, and made up to 1 litre. 10 c.c. required (30 − 14·4) = 15·6 c.c. $TiCl_3$(1 c.c. = 0·001745 grm. Fe) 123 nitrobenzene = 336 Fe

therefore 1·002 contain—

$$\frac{0\text{·}001745 \times 123 \times 15\text{·}6 \times 100}{336} = 0\text{·}9963 = 99\text{·}43 \%$$

Insoluble nitro compounds which are not easily sulphonated are best estimated by dissolving a known quantity in alcohol, and running this in a thin stream into a known volume of titanous chloride acidulated with HCl contained in a conical flask, into which carbon dioxide is passed. The mixture is boiled, then allowed to cool, and the excess of titanous chloride is estimated in the usual way. This method is useful for the valuation of compounds like dinitrobenzene, dinitronaphthalene, and trinitrotoluene.

EXAMPLE.—0·1002 grm., 1·8, *dinitronaphthalene*, $C_{10}H_6(NO_2)_2$ was dissolved in alcohol and the solution made up to 250 c.c.

50 c.c. $TiCl_3$ was measured into a conical flask, hydrochloric acid was added, CO_2 passed over, and 25 c.c. of the dinitronaphthalene solution run in. The mixture was boiled, then allowed to cool, and afterwards titrated back. Iron alum required = 31·55 c.c. $TiCl_3$.

Therefore the dinitronaphthalene solution required 18·45 ; but 25 c.c. alcohol alone required 0·8 c.c., so the dinitronaphthalene used 17·65 c.c. $TiCl_3$.

$$1 \text{ c.c. } TiCl_3 = 0·001742 \text{ grm. Fe}$$
$$218 \text{ dinitronaphthalene} = 672 \text{ Fe}$$

therefore 0·01002 grm. taken contains—

$$0·009974 \text{ grm.} = \mathbf{99·54} \%$$

Nitroso Compounds

The nitroso compounds can be titrated directly in hydrochloric acid solution. About 1 grm. of the nitroso compound is dissolved in hydrochloric acid and made up to 250 c.c. 50 c.c. of this solution are warmed over a Bunsen to about 40–50° C., CO_2 is passed into the flask, and the solution is then titrated with titanous chloride until the intense yellow colour is completely destroyed. Four equivalents of titanous chloride are required for the reduction of each nitroso group.

EXAMPLES.—*p. Nitrosodimethylaniline*, $C_6H_4N(CH_3)_2NO$.
50 c.c. solution prepared as above required 20·15 c.c. $TiCl_3$.

$$1 \text{ c.c. } TiCl_3 = 0·001476 \text{ grm. Fe}$$
$$150 \text{ nitrosodimethylaniline} = 224 \text{ Fe}$$

therefore 50 c.c. solution contain—

$$\frac{0·001476 \times 150 \times 20·15}{224} = 0·19914 \text{ grm.} = \mathbf{99·52} \%$$

p. Nitrosophenol, $NO . C_6H_4 . OH$.
0·335 grm. nitrosophenol was dissolved in water and the solution made up to 250 c.c.

25 c.c. of this solution were warmed to 40°, 10 c.c. conc. hydrochloric acid added and two drops dilute Methylene blue as indicator. Titrated at 30–40° C. with standard titanous chloride to colourless required 51·1 c.c. $TiCl_3$

$$1 \text{ c.c. } TiCl_3 = 0·001126 \text{ Fe}$$
$$123 \text{ nitrosophenol} = 224 \text{ Fe}$$

This gives 94·3 %

It is important that the exact conditions with regard to temperature should be strictly observed. Thus another portion of the same solution boiled for half an hour and then titrated gave only 61 %.

Diazo Compounds (p. 33)

The usual methods of estimating diazo compounds are well known, easy to carry out and give exact results. The new methods suggested are rather more difficult to manipulate, but may be found useful in certain contingencies.

EXAMPLES—1. *Diazobenzene chloride.* 10 c.c. of a solution of the diazo compound was cooled in a freezing mixture and 24·3 c.c. titanous chloride run in. After standing for about fifteen minutes while passing CO_2 through the flask, sodium tartrate was added and the excess of titanous chloride back-titrated with Acid green.

$$\text{Acid green required} = 7\cdot93 \text{ c.c. } TiCl_3$$
$$TiCl_3 \text{ used} = 16\cdot4 \text{ c.c.}$$
$$\text{1 c.c. } TiCl_3 = 0\cdot0068789 \text{ Fe}$$
$$\text{and as } 112 \text{ Fe} = 140\cdot5 \text{ } C_6H_5N_2Cl$$

the solution therefore contains 14·05 grms. per litre.

2. *Sodium paranitro isodiazobenzene.* 2·965 grms. nitrosamine paste was dissolved in water containing a little caustic soda and the solution made up to 250 c.c. 10 c.c. of this solution was taken, about 10 c.c. of a saturated solution of sodium tartrate added and 30 c.c. titanous chloride (1 c.c. = 0·002704 grm. Fe) run in. About 20 c.c. strong hydrochloric acid was added, the solution boiled for ten minutes while maintaining a current of CO_2 through the flask and the solution back-titrated with Crystal scarlet.

$$\text{Crystal scarlet required } 8\cdot2 \text{ c.c.}$$

$$\text{1 c.c. Crystal scarlet} = 0\cdot001395 \text{ grm. Fe}$$
$$\therefore \text{ } TiCl_3 \text{ used up} = 25\cdot77 \text{ c.c.}$$
$$\text{and as } 560 \text{ Fe} = 189 \text{ } NO_2 . C_6H_4 . N_2ONa$$

the paste therefore contains 19·7 % of this compound.

Quinones

A number of quinones may be estimated by direct titration with titanous chloride, using Methylene blue as indicator.

Benzo and toluquinones are dissolved in cold water, naphthoquinone is dissolved in alcohol or glacial acetic acid, but the former is to be preferred as a solvent for this purpose. About 0·25 to 0·1 grm. of substance is used for the estimation, and a suitable strength of Methylene blue to be used as indicator is 0·5 grm. per litre. One drop of this is added to the solution of quinone to be estimated, the titanous chloride not destroying the blue colour until all the quinone has been reduced.

EXAMPLE.—*Benzoquinone.* 0·0998 grm. was dissolved in water and made up to 100 c.c. ; 25 c.c. of the solution required 17·6 c.c. $TiCl_3$.

$$108 \; C_6H_4O_2 = 112 \; Fe$$
$$1 \; c.c. \; TiCl_3 = 0\cdot001408 \; grm. \; Fe$$
$$= 0\cdot001357 \; grm. \; quinone$$

therefore 25 c.c. solution contain—

$$0\cdot001357 \times 17\cdot6 = 0\cdot02388 \; grm.$$
$$= 95\cdot71 \; \% \; quinone$$

Volumetric Determination of Dyestuffs

Although most of the synthetic dyestuffs can be estimated with accuracy by means of titanous chloride, two important classes, the sulphide colours and the vat dyes (other than those for which methods are given) form exceptions. The difficulty experienced with these colours is that they cannot be sulphonated and thus rendered soluble in an acid medium ; reduction in a state of suspension, followed by back-titration (as with the insoluble nitro compounds) is of no use, since the leuco compounds would be thereby simply reoxidised to the original dyestuffs. Certain other dyestuffs of which Auramine, Acridine yellow and Primuline and its derivatives are technically the most important, cannot be reduced by titanous chloride, and this means is therefore not available for their estimation. Berberine, the colouring matter from ordinary barberry bark, is likewise not affected by titanous chloride.

Although titration with titanous chloride will give the exact amount of dyestuff present, providing that the composition is known and the product does not contain other dyestuffs in admixture, it is important to remember that in judging the quality of a commercial product, the purity and shade are also of importance. As these are not indicated by a titration, it is always advisable to carry out where this is practicable a quantitative dye-trial, to ascertain these attributes and to act as a check on the volumetric estimation.

The Estimation of Azo Dyes (p. 142)

Method I.—Azo dyes, which are not precipitated by dilute hydrochloric acid, may be titrated directly. This applies to colours like Orange II., Orange G, Scarlet 2G, Crystal scarlet 6R, Scarlet R, Fast red, etc. The azo group requires four equivalents of titanous chloride.

EXAMPLES.—1. *Crystal scarlet.* 0·5 grm. dyestuff was dissolved in distilled water and made up to 500 c.c. 100 c.c. were measured

H

into a conical flask, and after adding 10 c.c. concentrated hydrochloric acid, was boiled for about a minute and then titrated with titanous chloride, of which 17 c.c. was required.

$$1 \text{ c.c. } TiCl_3 = 0.001712 \text{ grm. Fe}$$
$$502 \; C_{20}H_{12}N_2O_7S_2Na_2 = 224 \text{ Fe}$$
$$\therefore \; \frac{0.001712 \times 17.1 \times 502}{224} = 0.06559 \text{ grm. colour}$$

and 1 grm. contains—

$$0.6559 \text{ Crystal scarlet} = 65.59 \%$$

2. *Scarlet* 2G.   0.5 grm. dissolved in 500 c.c.
100 c.c. solution required 23.1 c.c. $TiCl_3$(1 c.c. $TiCl_3$ = 0.001876 grm.Fe)
$$452 \; C_{16}H_{10}N_2O_7S_2Na_2 = 224 \text{ Fe}$$
therefore 100 c.c. solution contain—

$$0.08743 \text{ grm.} = 87.43 \%$$

Orange II.—1 grm. was dissolved in 500 c.c. water.   50 c.c. required 31.7 c.c. $TiCl_3$.

$$1 \text{ c.c. } TiCl_3 = 0.001554 \text{ grm. Fe}$$
$$350 \; C_{16}H_{11}N_2O_4SNa = 224 \text{ Fe}$$
therefore 50 c.c. solution contain—

$$\frac{0.001554 \times 350 \times 31.7}{224} \text{ grm.} = 0.07681 \text{ grm.}$$
$$= 76.81 \%$$

This estimation of azo dyes affords a ready method of determining the maximum quantity of any of these colours which is absorbed in dyeing wool.   The maximum amount of colour taken up by wool which has been dyed with 50 % Orange G, for example, is ascertained in the manner described below, and this serves to illustrate the mode of procedure.

1 grm. of wool was dyed for one hour with exactly 50 % of Orange G and 30 % sulphuric acid.   After the dyeing process was complete, and the wool had been removed from the bath, the latter was made up to 500 c.c., and 50 c.c. were titrated with titanous chloride (1 c.c. $TiCl_3$ = 0.001418 grm. Fe) ; 50 c.c. colour required 11.8 c.c. $TiCl_3$

$$452 \; C_{16}H_{10}N_2S_2O_7Na_2 = 224 \text{ Fe}$$
that is, $\dfrac{0.001418 \times 452 \times 11.8}{224} = 0.03376$ grm. Orange G

500 c.c. contain therefore 0.3376 grm. Orange G, and the wool has taken up 0.5 − 0.3376 = 0.1624 grm. = 16.24 %.

Method II.—Many of the azo dyes which are precipitated by hydrochloric acid can be titrated directly in the presence of Rochelle salt or sodium tartrate.

A known weight of the dyestuff is dissolved in water, and a definite volume of the solution, together with a solution of Rochelle salt, is titrated with titanous chloride.

The process has been found useful in the valuation of Diamine

black, Diamine violet, Benzo green, etc., and has been used successfully for pure Benzopurpurin and Erika, but commercial samples of these two dyestuffs do not always give distinct end reactions, and the indirect method (III.) of titrating these azo dyes is to be preferred for their exact valuation.

EXAMPLE.—1 grm. *Diamine black B.H.* was dissolved in water and made up to 250 c.c. 50 c.c. colour solution with 25 c.c. Rochelle salt (20 %) required 18·9 c.c. TiCl$_3$.

$$1 \text{ c.c. TiCl}_3 = 0 \cdot 001742 \text{ grm. Fe}$$
$$960 \text{ C}_{34}\text{H}_{24}\text{O}_{14}\text{N}_6\text{S}_4\text{Na}_4 = 448 \text{ Fe}$$

The solution contains therefore—

$$\frac{0 \cdot 001742 \times 960 \times 18 \cdot 9 \times 5}{448} = 0 \cdot 3518 \text{ grm.}$$
$$= 35 \cdot 25 \%$$

Method III.—The direct cotton yellows like Chrysophenine cannot be estimated with titanous chloride by direct titration, because acids precipitate them, and sodium tartrate forms a compound with titanium which in dilute solution is pale yellow, and obscures the end reaction in the titration of yellow colours by Method II. An indirect method is therefore applied. A known amount of colour solution is boiled in a conical flask into which carbon dioxide is passed, hydrochloric acid is added, and an excess of titanous chloride is run into the mixture. The contents of the flask are again boiled until the colour has been destroyed, which will usually take place in about two minutes, and the flask then cooled in an atmosphere of carbon dioxide which is maintained through the flask throughout the estimation. When cold, the excess of titanous chloride is estimated by titrating with standard iron alum solution ammonium—using sulpho- cyanide solution as indicator. By subtracting the number of c.c. of the iron alum solution (or their equivalent in titanous chloride, should the two solutions not be of equal strength) from the total number of c.c. of titanous chloride run in, the exact amount of the reducing agent used up by the dyestuff is arrived at.

EXAMPLES.—1. *Chrysophenine G.*, C$_{30}$H$_{26}$N$_4$O$_8$S$_2$Na$_2$. 1 grm. of the colour was dissolved in water and made up to 1 litre; 100 c.c. were boiled, hydrochloric acid was added, and 50 c.c. of titanous chloride. The mixture was boiled until all the precipitate dissolved and the solution acquired a slight violet tint, due to the excess of TiCl$_3$. It was then cooled by allowing a stream of water to circulate round the flask, and it was then titrated back with iron alum.

$$1 \text{ c.c. TiCl}_3 = 0 \cdot 001712 \text{ grm. Fe}$$
$$1 \text{ c.c. iron alum solution} = 1 \cdot 03 \text{ c.c. TiCl}_3$$
$$680 \text{ Chrysophenine} = 448 \text{ Fe}$$

100 c.c. Chrysophenine + 50 c.c. $TiCl_3$ required 25·2 c.c. iron alum.

$$25·2 \text{ iron alum} = 26·0 \text{ c.c. } TiCl_3$$

∴ amount of $TiCl_3$ used by Chrysophenine = 24 c.c.

therefore 0·1 grm. or 100 c.c. Chrysophenine solution contain—

$$\frac{0·001712 \times 680 \times 24}{448} = 0·06235 \text{ grm.}$$

$$= \mathbf{62·35 \%}$$

2. *Benzopurpurin 4B.*—1·005 grm. dissolved in 500 c.c.   50 c.c. reduced with titanous chloride 50 c.c.

$$1 \text{ c.c. } TiCl_3 = 0·001845 \text{ grm. Fe}$$
$$724 \; C_{34}H_{26}N_6S_2O_6Na_2 = 448 \text{ Fe}$$

required 30·2 c.c. iron alum (1 c.c. = 0·99 c.c. $TiCl_3$) = 29·9 c.c. excess $TiCl_3$ and 20·1 c.c. $TiCl_3$ used by Benzopurpurin.

$$\therefore 50 \text{ c.c. or } 0·1005 \text{ grm.} = \frac{0·001845 \times 724 \times 20·1}{448} = 0·05992 \text{ grm.}$$

$$= \mathbf{59·62 \%}$$

Diamine Sky Blue and Azo Compounds with H. Acid

Titanous chloride decolourises a solution of Diamine sky blue, but on exposure to air or when iron alum is added, the colourless solution assumes a red colour. This appears to be characteristic of the colouring matters prepared by combining diazo compounds with H. Acid in alkaline solution.

It is possible to estimate such colours as Fast acid magenta, Diamine sky blue, etc., by boiling in an atmosphere of carbon dioxide, adding excess of titanous chloride, and then titrating back with iron alum until· a faint red colour appears. For evidence of the quantitative reaction, see p. 43.

EXAMPLE.—0·942 grm. *Diamine sky blue* was dissolved in water and made up to 250 c.c.

25 c.c. was reduced with 20 c.c. $TiCl_3$.

Excess of $TiCl_3$ by iron alum = 7·6 c.c.

therefore 12·4 c.c. $TiCl_3$ was required by colour.

$$992 \; C_{34}H_{24}N_6O_{16}S_4Na_4 = 448 \text{ Fe}$$
$$1 \text{ c.c. } TiCl_3 = 0·001542 \text{ grm. Fe} = 0·003414 \text{ grm. colour}$$
$$\therefore 250 \text{ c.c. contain } 0·03414 \times 12·4 = 0·4233 \text{ grm. colour}$$
$$\text{or } \mathbf{44·9 \%}$$

Although the direct titration (Method I. for azo dyes) applies to colours of the same type as Fast acid magenta, and direct titration (Method II.) with sodium tartrate applies to Diamine sky blue, the indirect method described above is included as it is the one adopted in estimating Diamine sky blue on dyed cotton fabrics.

Tartrazine

1 grm. of the commercial product is dissolved in water and the solution is made up to 250 c.c. 50 c.c. of this solution are titrated directly in presence of hydrochloric acid with titanous chloride until the colour is destroyed.

EXAMPLE.—1·4405 grm. was dissolved in distilled water and the solution made up to 250 c.c. 50 c.c. was measured into a conical flask, hydrochloric acid added and after heating to the boil the solution titrated with titanous chloride until the yellow colour was no longer visible. The amount required was 20·7 c.c.

$$1 \text{ c.c. TiCl}_3 = 0·003315 \text{ grm. Fe}$$
$$534 \text{ C}_{16}\text{H}_9\text{N}_4\text{O}_9\text{S}_2\text{Na}_3 = 224 \text{ Fe}$$
$$250 \text{ c.c. contain } 0·8178 \text{ grm. dyestuff} = \mathbf{56·8} \%$$

DYESTUFFS YIELDING COLOURLESS LEUCO COMPOUNDS

Methylene Blue

1 grm. is dissolved in 250 c.c. water ; 50 c.c. is measured into a conical flask, a small quantity of hydrochloric acid is added, carbon dioxide is passed into the flask in the manner described for Indigo, and the contents are heated to about 35°. Titanous chloride is then run in until the blue colour just disappears.

$$\text{C}_{16}\text{H}_{18}\text{N}_3\text{SCl} + \text{H}_2 = \text{C}_{16}\text{H}_{20}\text{N}_3\text{SCl}$$
$$319·5 \text{ Methylene blue} = 112 \text{ Fe}$$

EXAMPLE.—0·97 grm. *Methylene blue* was made up to 250 c.c. 50 c.c. of this solution required 32·4 c.c. TiCl$_3$.

$$1 \text{ c.c. TiCl}_3 = 0·001563 \text{ grm. Fe}$$
$$= 0·004458 \text{ ,, Methylene blue}$$

therefore 50 c.c. or 0·194 grm. Methylene blue contains—

$$0·1444 \text{ grm. C}_{16}\text{H}_{18}\text{N}_5\text{SCl} = \mathbf{74·45} \%$$

Indigo

Pure Indigo can be estimated by titrating the sulphonated dyestuff with titanous chloride in the presence of sodium tartrate and in an atmosphere of carbon dioxide.

For this purpose 1 grm. of the finely ground sample is mixed with 5 c.c. pure sulphuric acid, and heated in a water-oven at 95° C. for one hour. The contents of the vessel are then cooled,

and are dissolved in water and made up to 500 c.c. 50 c.c. of this solution and 50 c.c. of sodium tartrate (20 % solution) is introduced into a conical flask fitted with a rubber stopper having three holes. Through one of them a current of carbon dioxide is introduced, another is fitted with a tube for the escape of the gas, and a third is left for the delivery tube of the titanous chloride burette (see Fig. 3). The solution is boiled and then titrated with titanous chloride. In this process the indigo is reduced to indigo white, and the solution assumes a yellow colour when the reaction is complete.

FIG. 3.

EXAMPLE.—50 c.c. Indigo solution prepared as above required when titrated in presence of sodium tartrate 21·30 c.c. $TiCl_3$.

$$1 \text{ c.c. } TiCl_3 = 0·0020 \text{ grm. Fe}$$
$$262 \ C_{15}H_{10}N_2O_2 = 112 \text{ Fe}$$

50 c.c. solution contain therefore—

$$0·09964 \text{ Indigo} = 99·64 \ \% \text{ indigotine}$$

Commercial Indigo usually contains impurities which are liable to interfere with the end reaction in this titration, and several processes have been devised by means of which the indigotine may either be isolated or freed from impurities, and in that condition it is possible to estimate the Indigo by titration with $TiCl_3$.

These purification processes include—

1. Grossmann's modification.[1]

1 grm. of Indigo is treated with 5 c.c. H_2SO_4(100 %) at 95° C. for one hour. The sulphonic acid is cooled, dissolved in about 400 c.c. water, and pure calcium carbonate is added until the solution is neutral; it is then made up to a convenient volume (e.g. 1 litre) and allowed to settle. An aliquot part is

[1] J. S. C. I., 1905, p. 308.

then decanted off and titrated with $TiCl_3$ as described for pure Indigo.

EXAMPLE.—100 c.c. indigo solution prepared as above required 12·8 c.c. $TiCl_3$.

$$1 \text{ c.c. } TiCl_3 = 0\cdot001695 \text{ grm. Fe}$$

therefore 100 c.c. contain—

$$\frac{0\cdot001695 \times 262}{112} = 0\cdot05075 \text{ Indigotine}$$

$$= 50\cdot75 \%$$

2. Bloxam's method [1] depends upon the production and isolation of indigotine tetrasulphonate of potash in the following way :—

1 grm. of Indigo is sulphonated by heating on a water-bath with 5 c.c. of 20 % fuming sulphuric acid for half an hour. The product is then poured into water and made up to 500 c.c. 100 c.c. are transferred to a large beaker, and 100 c.c. of a solution of potassium acetate (450 grms. per litre) added. The mixture is boiled, then cooled first in a stream of water and then with ice for one hour. Indigotine tetrasulphonate of potash separates out, and this is filtered off through a Gooch crucible. It is then washed with a solution prepared by adding 5 c.c. glacial acetic acid to 200 c.c. of the potassium acetate solution and 400 c.c. water, until the washings lose their brown colour and assume a pale blue tint. The tetrasulphonate is then dissolved in boiling water and titrated with titanous chloride in the manner described for pure indigo.

EXAMPLE.—The indigotine tetrasulphonate from 0·2 grm. indigo was dissolved in 100 c.c. water. 50 c.c. solution required 16·2 c.c. $TiCl_3$.

$$1 \text{ c.c. } TiCl_3 = 0\cdot001172 \text{ grm. Fe}$$

50 c.c. contain therefore—

$$\frac{0\cdot001712 \times 262 \times 16\cdot2}{112} = 0\cdot06558$$

$$= 65\cdot58 \%$$

3. Möhlau and Zimmermann's process. [2]

0·1 grm. of Indigo is heated with 100 c.c. glacial acetic acid and 5 c.c. concentrated sulphuric acid for twenty minutes on a water-bath, and the solution poured into water and filtered. The precipitate consists of finely divided crystallised indigotine, which can be filtered through a Gooch crucible, dried, sulphonated and titrated with titanous chloride.

[1] *J. S. C. I.*, 1906, p. 735.   [2] *Z. Farb. Text. Chem.*, 1903, p. 10.

The results obtained by this method are slightly high as compared with other processes.

EXAMPLE.—0·1 grm. required 18·2 c.c. TiCl$_3$.

$$1 \text{ c.c. TiCl}_3 = 0.001645 \text{ grm. Fe}$$

0·1 grm. Indigo contain therefore—

$$\frac{0.001645 \times 262 \times 18.2}{112} = 0.07003$$

$$= 70.03 \%$$

The error to which this method is liable has been pointed out by Grossmann and also by Bergtheil.

4. Purification with 80 % sulphuric acid.

This method is based upon the following observations :—

(a) Indigo is soluble in 80 % sulphuric acid, forming a sulphate which when poured into water dissociates with separation of indigotin as such. This sulphate has, according to Binz and Kufferath,[1] the composition $C_{16}H_{10}N_2O_2 . 2H_2SO_4$.

(b) That other products which may be present as impurities in Indigo are either soluble in 80 % sulphuric, but remain in solution on the addition of water, or they do nòt yield to the subsequent sulphonation process.

This process, which has proved to be a convenient one, is carried out in the following way :—

0·2 grm. Indigo is treated with about 10 c.c. of 80 % sulphuric acid for a quarter of an hour with frequent stirring, and the temperature is maintained at about 40° C. 100 c.c. water is then added, and after boiling, the Indigo is filtered through a Gooch crucible. The filtering medium may be either sand and asbestos or preferably a filter bed about ⅓ in. deep, consisting of a layer of coarsely crushed quartz, then finer quartz, and as the upper layer a little finely divided silica.

The precipitate is washed, dried, and sulphonated with ordinary sulphuric acid in the usual way. It is then dissolved in water and titrated with titanous chloride in the presence of sodium tartrate and in an atmosphere of carbon dioxide.

EXAMPLES.—1. *Artificial Indigo.*

$$1 \text{ c.c. TiCl}_3 = 0.001982 \text{ grm. Fe}$$

0·2 grm. Indigo required 40·1 c.c. TiCl$_3$;

therefore 0·2 grm. contains—

$$\frac{0.001982 \times 262 \times 40.1}{112} = 0.1859 \text{ grm.}$$

$$= 92.95 \%$$

[1] *Ann.*, 1903, 325.

2. *Artificial Indigo paste.*

1 c.c. $TiCl_3$ = 0·001864 grm. Fe

0·2 grm. Indigo required 12·1 c.c. $TiCl_3$; therefore 0·2 grm. contains—

$$\frac{0·001884 \times 12·1 \times 262}{112} = 0·04199 \text{ grm.}$$

$$= 20·99 \%$$

3. *Natural Indigo.*

1 c.c. $TiCl_3$ = 0·002013 grm. Fe

0·2 grm. Indigo required 20·1 c.c. $TiCl_3$; therefore 0·2 grm. contains—

$$\frac{0·002013 \times 20·1 \times 262}{112} = 0·09465 \text{ grm.}$$

$$= 47·33 \%$$

Magenta

1 grm. of this dyestuff is dissolved in 500 c.c. water. 50 c.c. of this solution and 25 c.c. of a 20 % Rochelle salt solution (or sodium tartrate) are boiled and then titrated in a current of carbon dioxide.

EXAMPLE.—0·969 grm. *Magenta* was dissolved in water and made up to 500 c.c. 50 c.c. of this solution required 15·5 c.c. $TiCl_3$.

1 c.c. $TiCl_3$ = 0·001724 grm. Fe

323·5 $C_{19}H_{18}N_3Cl$ = 112 Fe

∴ 1 c.c. $TiCl_3$ = 0·004979 grm. p. rosaniline hydrochloride

0·0969 grm. contains 0·007717 grm.

= 79·64 % *calculated as p. rosaniline hydrochloride,* $C_{19}H_{18}N_3Cl$

or 83·06 % *calculated as rosaniline hydrochloride,* $C_{20}H_{20}N_3Cl$

Acid Magenta

The commercial product is the sodium salt of the trisulphonic acid of magenta. It is titrated in exactly the same way as magenta.

EXAMPLE.—1 grm. *Acid Magenta* was dissolved in water and made up to 100 c.c. 50 c.c. solution required 24·1 c.c. $TiCl_3$.

611 $C_{19}H_{16}N_3O_{10}S_3Na_3$ = 112 Fe

or 625 $C_{20}H_{18}N_3O_{10}S_3Na_3$ = 112 Fe

1 c.c. $TiCl_3$ = 0·001821 grm. Fe

50 c.c. colour contain 0·01016 × 24·1 = 0·2448

rosaniline trisulphonate of soda = 48·96 %

or *pararosaniline trisulphonate of soda* = 47·88 %

Eosin A

When Eosin is treated with titanous chloride in the presence of Rochelle salt decolourisation ensues, but the solution becomes turbid owing probably to the separation of the leuco compound. In consequence of this the end reaction is indistinct. By adding an equal volume of alcohol to the solution before titrating, a definite end reaction is obtained, and the solution becomes yellow on reduction.

EXAMPLE.—1·04 grm. *Eosin A* was dissolved in water and the solution made up to 250 c.c. 50 c.c. of this solution was mixed with 25 c.c. Rochelle salt solution (20 %) and 50 c.c. alcohol. Carbon dioxide was passed over the solution, which was then boiled and titrated with titanous chloride.

$$1 \text{ c.c. } TiCl_3 = 0\cdot001672 \text{ grm. Fe}$$
50 c.c. Eosin solution required 10·2 c.c. $TiCl_3$.
$$689\cdot6 \text{ A, } C_{20}H_6O_5Br_4Na_2 = 112 \text{ Fe}$$
$$1 \text{ c.c. } TiCl_3 = 0\cdot010294 \text{ grm. Eosin}$$
50 c.c. or 0·20 grm. Eosin solution contains 0·1049 grm.
$$= \mathbf{50\cdot46 \%}$$

Rhodamine

This colour is estimated in the same way as Eosin.

EXAMPLE.—1·01 grm. Rhodamine B was dissolved in water and made up to 250 c.c. 50 c.c. colour solution, 25 c.c. Rochelle salt, and 50 c.c. alcohol were boiled in an atmosphere of carbon dioxide, and titrated with titanous chloride; required 10·6 c.c. (1 c.c. $TiCl_3 = 0\cdot001901$ grm. Fe).

$$478\cdot5 \; C_{28}H_{31}N_2O_3Cl = 112 \text{ Fe}$$
$$\therefore 1 \text{ c.c. } TiCl_3 = 0\cdot008121 \text{ grm. Rhodamine}$$
50 c.c. or 0·202 grm. contains 0·08609 grm. Rhodamine
$$= \mathbf{42\cdot61 \%}$$

Phenol Phthalein

The titration is effected in alcoholic solution in presence of sodium tartrate.

EXAMPLE.—0·1992 grm. of a commercial product was dissolved in alcohol and after the addition of sodium tartrate was titrated hot with titanous chloride in a current of CO_2 until a spot taken out on a glass rod no longer gave a red colour with caustic soda.

$$TiCl_3 \text{ required } 33\cdot4 \text{ c.c.}$$
$$1 \text{ c.c. } TiCl_3 = 0\cdot001823 \text{ grm. Fe}$$
$$318 \; C_{20}H_{14}O_4 = 112 \text{ Fe}$$
This gives **86·7 %** phenol phthalein.

Gallein

A known weight of the dyestuff is dissolved in alcohol, sodium tartrate added and the solution titrated with titanous chloride at or near the boil while passing a current of CO_2 through the flask. The end of the reaction is indicated by the change from magenta to pale yellow.

EXAMPLE.—0·3450 grm. commercial gallein paste was dissolved in alcohol and titrated as described.

$$TiCl_3 \text{ required } 15\cdot3 \text{ c.c.}$$
$$1 \text{ c.c. } TiCl_3 = 0\cdot002215 \text{ grm. Fe}$$
$$364 \ C_{20}H_{12}O_7 = 112 \text{ Fe}$$

This gives **31·8** % gallein.[1]

Malachite Green

The titration of this dyestuff is carried out in exactly the same manner as described for Magenta. This product behaves in a somewhat different manner towards the reducing agent, however. After the addition of 3 to 4 c.c. of the titanous chloride solution the colour disappears momentarily, returns again, and then disappears in the same way with the next addition, and it is only when the reaction is complete that the colour no longer reappears.

EXAMPLE.—1·12 grm. *Malachite green* was dissolved and made up to 250 c.c. with water ; 50 c.c. was taken, along with 25 c.c. Rochelle salt, and was found to require 23 c.c. $TiCl_3$

$$1 \text{ c.c. } TiCl_3 = 0\cdot001645 \text{ grm. Fe}$$
$$926 \ (2 \ C_{23}H_{24}N_2 + 3 \ C_2H_2O_4) = 224 \text{ Fe}$$
$$\therefore 1 \text{ c.c. } TiCl_3 = 0\cdot00680 \text{ grm. Malachite green}$$

50 c.c. solution or 0·224 grm. contains 0·1564 grm. Malachite green
$$= \mathbf{69\cdot82} \ \%$$

Aniline Blue

Pure triphenyl pararosaniline is prepared by heating pararosaniline with freshly distilled aniline and a little benzoic acid. The melt is treated with excess of hydrochloric acid, and the hydrochloride is then filtered off, washed with water, and recrystallised from alcohol.

The product obtained in this way has the formula corre-

---

[1] This high percentage of colour was due to the paste having become almost solid through loss of water.

sponding to triphenyl pararosaniline, and may be estimated in the following way :—

The product is first sulphonated for an hour with concentrated sulphuric acid at 100° C. made up to a known volume with water, and then an aliquot part of this is mixed with Rochelle salt or sodium tartrate, and is titrated in an atmosphere of carbon dioxide with titanous chloride.

EXAMPLE.—0·495 grm. *Triphenyl pararosaniline* was sulphonated with 5 c.c. conc. H_2SO_4 and made up to 250 c.c. with water ; 50 c.c. of this solution required 10·7 c.c. $TiCl_3$

$$1 \text{ c.c. } TiCl_3 = 0\cdot001869 \text{ grm. Fe}$$
$$551\cdot5 \; C_{37}H_{30}N_3Cl = 112 \text{ Fe}$$
∴ 50 c.c. or 0·099 grm. sample contains 0·09847 grm. $C_{37}H_{30}N_3Cl$
$$= 99\cdot46 \%$$

The Aniline blue of commerce consists mainly of diphenyl-rosaniline and di- and tri-phenylpararosaniline.

Safranine

In the titration of this dyestuff it has been found necessary to use sodium bitartrate instead of Rochelle salt in the estimation. In other respects the estimation of this dyestuff resembles the process described for Magenta.

EXAMPLE.—1 grm. of *Tolusafranine* was dissolved in 250 c.c. water ; 50 c.c. was measured into a conical flask, 25 c.c. of a saturated solution of sodium bitartrate were added, the mixture was boiled and titrated with titanous chloride in an atmosphere of carbon dioxide.

50 c.c. safranine solution required 24·2 c.c. $TiCl_3$.

$$1 \text{ c.c. } TiCl_3 = 0\cdot001642 \text{ grm. Fe}$$
$$364\cdot5 \; C_{21}H_2N_4Cl = 112 \text{ Fe}$$
50 c·c. or 0·2 grm. contain 0·1293 grm. Safranine $= 64\cdot65 \%$

Indoïne

This dyestuff, which is prepared by combining diazotised Safranine with β naphthol, is first reduced by titanous chloride to Safranine, and the latter is then further reduced to the leuco compound. The mode of procedure is exactly the same for the analysis of Indoïne as that described for Safranine. The azo group requires four and the Safranine two equivalents of hydrogen for reduction, making a total of six, or 6 Fe.

EXAMPLE.—0·5 grm. *Indoïne* dissolved in 500 c.c.; 50 c.c. required with bitartrate of soda 18·1 c.c. $TiCl_3$.

$$1 \text{ c.c. } TiCl_3 = 0 \cdot 001529 \text{ grm. Fe}$$
$$519 \cdot 5 \ C_{31}H_{26}N_5OCl = 336 \text{ iron}$$

therefore 50 c.c. contain—

$$\frac{0 \cdot 001529 \times 519 \cdot 5 \times 18 \cdot 1}{336} = 0 \cdot 4287 \text{ grm.}$$

$$= \mathbf{85 \cdot 56 \ \%} \text{ indoïne}$$

Alizarin S. (For Alizarin and allied dyestuffs, see p. 54.)

The titration of this dyestuff is effected in aqueous solution.

EXAMPLE.—0·1134 grm. of a commercial product was dissolved in water and heated to the boil, with the addition of sodium tartrate. Carbon dioxide was passed into the flask and 40 c.c. $TiCl_3$ added. After reduction the excess of $TiCl_3$ was ascertained by titrating back with iron alum of which 22·2 c.c. were required to destroy the blue colour.

$$22 \cdot 2 \text{ c.c. iron alum} = 22 \cdot 9 \text{ c.c. } TiCl_3$$

and $40 - 22 \cdot 9 = 17 \cdot 1$ c.c. was therefore used in reducing the Alizarin S.

$$1 \text{ c.c. } TiCl_3 = 0 \cdot 003166$$
$$240 \ C_{14}H_7O_7SNa = 224 \text{ Fe}$$

and 0·1134 contains 0·05783 grm. = 50·1 %

Estimation of Indigo in Dyed Cotton Fabrics

About 4 grms. of the dyed cotton are cut up into small pieces and placed in a porcelain beaker; 25 c.c. H_2SO_4 80 % strength (148° Tw.) is now added, and the whole is stirred slowly, the temperature being maintained at about 40° C. In a very short time the cotton begins to dissolve, and in about ten minutes it has all gone into solution. The contents of the beaker are now diluted with water to about 120 c.c. By treatment with sulphuric acid of 148° Tw. cellulose is converted into dextrin, which remains in solution on diluting with water, while the Indigo is converted into a sulphate, which on diluting with water dissociates with the separation of indigotine as such. This is filtered off through a Gooch crucible containing a filtering medium of quartz and silica. It is best to use as the bottom layer quartz crushed about the size of millet seeds, then a layer of finer quartz about the fineness of grain sugar, and lastly a layer of finely divided silica. The Indigo is washed with water,

dried, and then sulphonated and titrated in the manner described for pure Indigo.

The time required for a complete estimation is a little over two hours.

EXAMPLES.—1. 4·425 grms. indigo-dyed cotton was treated by the 80 % sulphuric process, and the Indigo residue was sulphonated and titrated as described ; 17·75 c.c. $TiCl_3$ were required.

$$1 \text{ c.c. } TiCl_3 = 0.001845 \text{ grm. Fe}$$
$$\text{Indigo on fibre} = \frac{0.001845 \times 262 \times 17.75}{112}$$
$$= 0.07662$$
$$= \mathbf{1.73\ \%}$$

2. 3·8 grm. indigo-dyed cotton was treated by the 80 % sulphuric process, and the Indigo residue was sulphonated and titrated as described ; 26·2 c.c. $TiCl_3$ were required.

$$1 \text{ c.c. } TiCl_3 = 0.001712 \text{ grm. Fe}$$
$$\text{Indigo on fibre} = \frac{0.001712 \times 262 \times 26.2}{112}$$
$$= 0.10493$$
$$= \mathbf{2.76\ \%}$$

The colours used for topping Indigo are usually either Methyl violet or Safranine, and if present will remain in solution in the sulphuric acid on diluting with water.

Of colours used for bottoming, the sulphide colours are destroyed either by the first or second treatment with sulphuric acid. Manganese bronze, if found present, is removed from the fibre with bisulphite of soda and sulphuric acid. Diamine black B.H. dissolves in 80 % sulphuric, and appears to be precipitated on diluting. In sulphonating, however, the colour is destroyed, and gives a brown precipitate on diluting. This substance does not, however, affect the accuracy of the Indigo estimation. Columbia black and Benzopurpurine 4B are apparently not destroyed in the sulphonating process, but are completely precipitated on diluting with water, so that they can be easily separated by filtration before titrating. Other colours, like Diamine sky blue and Diaminogene are to some extent soluble in acid, and if not detected may give rise to erroneous results. In case direct cotton colours have been detected in the preliminary examination of the dyed fabric, the safest plan to adopt is to wash the precipitated indigo, after filtration, with dilute ammonia, when any direct cotton colour will at once be rendered completely soluble, and will be carried into the filtrate. Thio-indigo red and other vat dyes such as Ciba blue, Indanthrene

blues, the Algol colours, etc., do not sulphonate with ordinary sulphuric acid, and if present in the fabric would consequently not interfere with the volumetric estimation of the indigotine.

Estimation of Alizarin in Cotton-dyed Turkey Red

The following mode of procedure has been adopted for the estimation of the Alizarin in Turkey red (free from arsenic) :—

From 1·5 to 3 grms. of the dyed cotton is cut up into small pieces and placed in a porcelain beaker.   About 10 c.c. 80 % H_2SO_4 is now added, and the whole stirred slowly.   The beaker may be slightly warmed, but in no case should the temperature be allowed to rise above 40° C., since above this temperature charring may take place, and the Alizarin is liable to be destroyed. In about twenty minutes all the cotton has dissolved, and a bright red viscous solution is obtained.   The contents of the beaker are now diluted with water to about 100 c.c. and stirred well.   By this means most of the Alizarin is precipitated in bright yellow flakes, only a small amount remaining in solution.   The precipitated Alizarin is filtered off, washed, dissolved in alcohol, and titrated in the manner described for pure Alizarin.   The filtrate from the precipitated Alizarin is of a bright yellow colour, and is titrated directly for the Alizarin it contains by adding, in an atmosphere of carbon dioxide, an excess of titanous chloride, boiling, cooling, adding sulphocyanide, and titrating back with iron alum.

In case the alumina mordant for the Turkey red has been fixed by means of arseniate of soda, the result is unreliable.

EXAMPLE.—2·28 grms. of Turkey red yarn was treated by the 80 % sulphuric acid process, and the Alizarin precipitated was obtained in alcoholic solution and titrated as described ; 17·6 c.c. TiCl$_3$ were required.   For the Alizarin in solution in the filtrate 0·75 c.c. TiCl$_3$ was required.

Total TiCl$_3$ used = 18·35 c.c.

$$1 \text{ c.c. TiCl}_3 = 0\text{·}001717 \text{ grm. Fe} = \frac{0\text{·}001717 \times 240}{224}$$

$$= 0\text{·}00184 \text{ grm. Alizarin}$$

therefore 18·35 c.c. TiCl$_3$ = 0·0337 grm. Alizarin and percentage of Alizarin on the fibre is **1·48**.

Estimation of Direct Cotton Colours on the Fibre

The dyed cotton is titrated directly with an excess of titanous chloride, which is afterwards titrated back with iron alum.

The process is carried out in a manner similar to the indirect method described for estimation of direct colours in solution.

A weighed quantity of the material is placed in a flask and first boiled with dilute hydrochloric acid. Carbon dioxide is then passed over, and an excess of titanous chloride is run in. The flask is heated over a Bunsen flame until all the colour has disappeared, when it is cooled, and the excess of titanous chloride is titrated back with iron alum, using sulphocyanide as indicator. Generally speaking, 5 grms. of cotton is a convenient quantity to use for each estimation, with titanous chloride of the usual strength (1 c.c. = 0·0015 to 0·002 grm. Fe). Equally good results have been obtained, however, with 1·5 grm. cotton and titanous chloride made up so that 1 c.c. = about 0·0003 grm. Fe.

The method can be employed for direct cotton azo dyes, and has been proved quantitative in the case of Benzopurpurin 4B, Congo red, Erika, Chrysophenin and Brilliant yellow.

EXAMPLES.—1·5 grms. cotton dyed with 3 % Benzopurpurin 4B (0·15 grm.). The colour was estimated in the bath and in the fibre by the process explained above. The colour on the fibre and in solution was reduced with 50 c.c. $TiCl_3$ in each case.

Excess $TiCl_3$ found in case of fibre, 22·95 c.c.

„   „   „   „   solution, 23·1 c.c. (by iron alum).

$$1 \text{ c.c. } TiCl_3 = 0 \cdot 001724 \text{ grm. Fe}$$
$$= \frac{0 \cdot 001724 \times 724}{448} = 0 \cdot 002786 \text{ grm. Benzopurpurin}$$

$$(50 - 22 \cdot 95) = 27 \cdot 05 \text{ c.c. } TiCl_3$$
$$= 0 \cdot 002786 \times 27 \cdot 05$$
$$= 0 \cdot 07536 \text{ grm. Benzopurpurin on fibre}$$

$$(50 - 23 \cdot 10) = 26 \cdot 9 \text{ c.c. } TiCl_3$$
$$= 0 \cdot 002786 \times 26 \cdot 9$$
$$= 0 \cdot 07486 \text{ grm. Benzopurpurin in solution}$$

Total colour on fibre and in solution $\Big\} = 0 \cdot 07536 + 0 \cdot 07486$

$$= 0 \cdot 1502 \text{ grm.}$$

2. 1·5 grm. cotton dyed with 0·5 % Benzopurpurin (0·0075 grm.). 25 c.c. $TiCl_3$ used in the case of fibre, and also for solution.

Excess $TiCl_3$ found in case of fibre, 16·7 c.c. (by iron alum).

„   „   „   „   solution 18·9 c.c.

That is, 8·3 c.c. $TiCl_3$ used by Benzopurpurin on fibre.

„   6·1 c.c.   „   „   „   in solution.

$$1 \text{ c.c. } TiCl_3 = 0 \cdot 000324 \text{ grm. Fe}$$
$$= \frac{0 \cdot 000324 \times 724}{448}$$
$$= 0 \cdot 0005236 \text{ grm. Benzopurpurin}$$

∴ 0·0005236 × 8·3 = 0·004346   „   „   on fibre

0·0005236 × 6·1 = 0·003194   „   „   in solution

3. 5 grms. cotton dyed with 2 % Chrysophenin G (0·1 grm.). Colour on fibre and in solution reduced separately with 50 c.c. TiCl₃ in each case.

Excess TiCl₃ found in case of fibre 39·6 c.c., and in the case of the solution 20·8 c.c. (by iron alum).

$$1 \text{ c.c. TiCl}_3 = 0 \cdot 001658 \text{ grm. Fe}$$
$$= \frac{0 \cdot 001658 \times 680}{448}$$
$$= 0 \cdot 002516 \text{ Chrysophenin}$$
$$(50 - 39 \cdot 6) = 10 \cdot 4 \text{ c.c. TiCl}_3$$
$$= 0 \cdot 002516 \times 10 \cdot 4$$
$$= 0 \cdot 02616 \text{ grm. Chrysophenin on fibre}$$
$$(50 - 20 \cdot 8) = 29 \cdot 2 \text{ c.c. TiCl}_3$$
$$= 0 \cdot 002516 \times 29 \cdot 2$$
$$= 0 \cdot 07347 \text{ grm. Chrysophenin in solution}$$

Methylene Blue in Dyed Cotton Fabrics

This determination is essentially the same as the estimation of the colour itself. A known weight of the cotton, cut up into small bits, is placed in a flask with water and hydrochloric acid, a current of carbon dioxide is passed into the flask, and the colour is titrated with titanous chloride. It is not always an easy matter to determine the exact point at which the dye is completely decolourised when present on the fibre, and it is consequently preferable to titrate with excess of titanous chloride, and then to titrate back with iron alum as for direct cotton colours. In this case, however, the colour acts as its own indicator, and no sulphocyanide is required.

EXAMPLE.—10 grms. dyed cotton was titrated as above, and found to require 11·15 c.c.

$$1 \text{ c.c. TiCl}_3 = 0 \cdot 001563 \text{ grm. Fe}$$
$$= 0 \cdot 004458 \text{ grm. Methylene blue}$$
$$\therefore 10 \text{ grms. cotton contain } 0 \cdot 004458 \times 11 \cdot 15$$
$$= 0 \cdot 04971 \text{ grm. Methylene blue}$$
$$= \mathbf{0 \cdot 497} \text{ \% Methylene blue}$$

Estimation of the Degree of Mercerisation in Cotton Yarns [1]

If the yarn is dyed, the colour should be previously stripped by suitable means, e.g. by treatment with acid and then with soda (mordant dyes), or by means of bleaching powder (basic and sulphide colours) or of titanous chloride (azo dyes).

[1] J. S. D. and C., 1908, p. 68.

I

The weighed sample of cotton under investigation (from 1 to 5 grms.) is dyed together with a weighed quantity of ordinary bleached cotton yarn by boiling for about twenty minutes in a bath containing Benzopurpurin 4B in excess, and after rinsing slightly the amounts of colour taken up by each are estimated by the method detailed above. The figures obtained are compared with those given in the table below ; these must, however, not be regarded as absolute, but as proportional values. Thus it may be found that in this determination the ordinary cotton has taken up less than 1·77 % of colour (the concentration of the dye liquor being the main contributing factor), and it therefore becomes necessary to calculate by proportion, from the amount of colour found on the ordinary yarn and that under examination, how much colour the sample would have absorbed if the amount taken up by the ordinary cotton was 1·77 %.

EXAMPLE.—5 grms. ordinary and 5 grms. mercerised cotton yarn was dyed in one bath with 4 % Benzopurpurin 4B. The samples were then taken out, rinsed slightly, and the colour estimated in each. The ordinary yarn was found to contain 1·405 % colour, and the mercerised 2·628 %.

If the ordinary yarn had taken up 1·77 % colour, then, by simple proportion, the mercerised yarn would have taken up 3·31 %. By reference to the table, it is seen that the mercerised yarn had been treated with caustic soda of about 50° Tw. strength.

Table showing the amounts of Benzopurpurin 4B taken up from the same bath by ordinary cotton and by cotton mercerised under tension in different strengths of caustic soda.

Strength of caustic soda.	Amount of colour taken up.	Strength of caustic soda.	Amount of colour taken up.
Untreated	1·77 %	45° Tw.	3·27 %
10° Tw.	1·88 ,,	50° ,,	3·38 ,,
20° ,,	2·39 ,,	55° ,,	3·50 ,,
25° ,,	2·57 ,,	60° ,,	3·56 ,,
30° ,,	2·95 ,,	65° ,,	3·60 ,,
35° ,,	3·02 ,,	70° ,,	3·66 ,,
40° ,,	3·15 ,,		

It should be noted that the figures given in the table only apply to cotton yarn mercerised *under tension*. If the mercerising has been done without tension, the amounts of Benzopurpurin taken up are considerably greater. It is furthermore important to bear in mind that mercerised cotton, when dried at an elevated

temperature, loses much of its characteristic affinity for colouring matters.[1] It is probably on this account that the above-mentioned process (likewise the iodine test) usually fails to give reliable results when applied to mercerised cotton piece goods, since these are generally dried over steam-heated cylinders, and are thus exposed to temperatures which materially alter some of the characteristic properties of the fibre, including its affinity for colouring matters.

CARBOHYDRATES

I. Glucose

For this estimation, Fehling's solution prepared in the following way is required :—

34·64 grms. $CuSO_4 . 5H_2O$ is dissolved in water and made up to 500 c.c.

51·6 grms. caustic soda and 173 grms. Rochelle salt are dissolved, mixed, and made up to 500 c.c.

Equal volumes of each of these solutions are used in the estimations. 100 c.c. of this solution is equivalent to 0·7787 grm. Fe.

50 c.c. of a 1 % solution of the sugar is added to 100 c.c. of Fehling's solution, and the mixture is boiled for two minutes ; 100 c.c. of cold water are then added, and the cuprous oxide is filtered off. The filtrate is acidified and made up to a known volume (500 c.c.). An aliquot part (25 c.c.) is titrated with titanous chloride, and in that way the amount of copper remaining in the filtrate is ascertained. (This process is carried out in the manner described for the estimation of copper, see p. 13.) The amount of copper reduced by the glucose is found by difference, and from this the amount of glucose is calculated from the factor. 0·3464 grm. $CuSO_4 . 5H_2O$ is completely reduced by 0·05 grm. glucose, or since one of iron is equivalent to one of copper sulphate, 1 grm. Fe = 0·6416 grm. glucose.

EXAMPLES

1. *Estimation of glucose by Fehling's solution.*—Amount of glucose taken, 1·051 grm. This was dissolved and made up to 100 c.c. ; 50 c.c. glucose solution was treated with 100 c.c. Fehling's solution as described. The cuprous oxide was filtered off, and the filtrate was made up to 500 c.c. ; 100 c.c. of this solution was titrated with

[1] *J. S. D. and C.*, 1908, p. 107.

titanous chloride in order to estimate the copper precipitated. The solution required 16·2 c.c. $TiCl_3$.

$$\text{I c.c. } TiCl_3 = 0\text{·}002013 \text{ grm. Fe}$$
$$16\text{·}2 \text{ c·c. } TiCl_3 = 16\text{·}2 \times 0\text{·}002013 = 0\text{·}03261 \text{ grm. Fe in 100 c.c.}$$
$$\text{or } 0\text{·}16305 \text{ in } 500 \text{ c.c.}$$

The extent of the reduction is therefore

$$0\text{·}7787 - 0\text{·}1630 = 0\text{·}6157 \text{ grm. Fe}$$
and since I grm. Fe = 0·6416 grm. glucose
$$0\text{·}6157 \text{ grm. Fe} = 0\text{·}6157 \times 0\text{·}6416 = 0\text{·}3950 \text{ grm. glucose in 50 c.c.}$$
$$\text{or } 0\text{·}79 \text{ grm. glucose in 100 c.c.}$$
$$1\text{·}05 \text{ contains } 0\text{·}79 = \mathbf{75\text{·}23} \%$$

2. *Estimation of glucose by the " absolute " method* (see p. 38).

1·130 grms. of a commercial white glucose was dissolved in water and the solution made up to 250 c.c. To 10 c.c. of this solution about I c.c. of pure phenylhydrazine dissolved in acetic acid was added, along with 2 c.c. saturated sodium tartrate solution, the whole being heated in a water bath for ten minutes; 50 c.c. $TiCl_3$ was added, the solution boiled for one minute, while passing a current of CO_2, when excess of HCl was added and the excess of $TiCl_3$ titrated back with standard Crystal scarlet.

$TiCl_3$ used up 27·4 c.c.

I c.c. $TiCl_3 = 0\text{·}002793$ grm. Fe, and as 180 glucose = 336 Fe, this gives **90·9** %.

II. Cane Sugar

This must first be inverted, the process being suitably carried out in the following manner :—

50 c.c. of a 10 % solution of sugar is measured into a 500 c.c. flask, and 5 c.c. pure hydrochloric acid added.

The flask is warmed on a water-bath to 65° C. with frequent shaking for ten minutes. The subsequent procedure is the same as in the estimation of glucose.

0·3464 grm. $CuSO_4 . 5H_2O$ is completely reduced by 0·0475 grm. cane sugar, or I grm. Fe = 0·6097 grm. cane sugar after inversion.

EXAMPLE.—3·764 grms. *sugar* dissolved and inverted as described were made up to 500 c.c. ; 50 c.c. treated with 100 c.c. Fehling's solution and filtered ; filtrate made up to 500 c.c. 50 c.c. of this solution required 8·4 c.c. $TiCl_3$.

$$\text{I c.c. } TiCl_3 = 0\text{·}002032 \text{ grm. Fe}$$
$$8\text{·}4 \text{ c.c. } TiCl_3 = 8\text{·}4 \times 0\text{·}002032 = 0\text{·}01707 \text{ grm. Fe in 50 c.c.}$$
$$\text{or } 0\text{·}1707 \text{ in } 500 \text{ c.c.}$$

The extent of the reduction is therefore

$$0\text{·}7787 - 0\text{·}1707 = 0\text{·}6080 \text{ grm. Fe}$$
and since I grm. Fe = 0·6097 grm. cane sugar (inverted)
$$0\text{·}6080 \text{ grm. Fe} = 0\text{·}6080 \times 0\text{·}6097 = 0\text{·}3696 \text{ grm. cane sugar in 50 c.c.}$$
$$\text{or } 3\text{·}764 \text{ grms. of the sugar contain } 3\text{·}696 \text{ grm.}$$
$$= \mathbf{98\text{·}3} \% \text{ cane sugar.}$$

Reducing Values of Cellulosic Substances

EXAMPLES.—*Determination of the reducing value of an oxidised cellulose.*

1. *By means of Fehling's solution.*

The oxidised cellulose used in this example had been obtained by oxidising cellulose (filter-paper) with one atomic proportion of oxygen on $C_6H_{10}O_5$ by the acid permanganate method. 2·698 grms. of the finely powdered air dry product [1] were heated to the boil with 250 c.c. distilled water in a 1½-litre flask fitted with a centrifugal stirrer. 100 c.c. of boiling Fehling's solution were introduced and the boiling maintained for fifteen minutes. 1 grm. of purified kieselguhr was then added and the liquid filtered at the pump, washing the residue with hot distilled water until the filtrate was free from copper. The filter and contents were then transferred to a vessel containing excess of iron alum, dissolved in dilute sulphuric acid. On warming, the cuprous oxide dissolved rapidly. The solution was filtered, the residue washed and the ferrous sulphate formed titrated with permanganate

$$56\cdot4 \text{ KMnO}_4 \text{ used}$$
$$1 \text{ c.c. KMnO}_4 = 0\cdot0055 \text{ grm. Fe} = 0\cdot00624 \text{ grm. Cu}$$

∴ 100 grms. air dry product reduces 13·3 grms. copper.

Allowing for moisture at 100°, the copper value would be 14·2, according to Schwalbe's definition. This figure includes, however, the hydrate copper number.

The estimation of the unreduced copper in the filtrate from the first operation was effected as follows: The filtrate and washings were strongly acidified with hydrochloric acid and made up to 1 litre. 50 c.c. of this solution with 10 c.c. of iron alum (1 c.c. = 0·001096 grm. Fe) required 31·9 c.c. TiCl₃. In a blank titration 5 c.c. of Fehling's solution with 10 c.c. iron alum required 46·6 c.c. TiCl₃. By difference this gives a copper value of 13·6. Deducting the copper value found by the permanganate process this gives 0·3 for the hydrate copper number.

2. *By means of Rosinduline.*

0·3813 grm. of powdered air dry oxycellulose was boiled for fifteen minutes with 40 c.c. of a 10 % caustic soda solution and 100 c.c. of a solution of Rosinduline G. The boiling was done in a stoppered conical flask with capillary outlet, a rapid stream of hydrogen being passed through the flask. The dark red solution was acidified by adding tartaric acid and the unreduced

[1] *J. S. D. and C.*, 1920, p. 251.

dyestuff was titrated with titanous chloride in an atmosphere of carbon dioxide.

$$39\text{·}1 \text{ c.c. TiCl}_3 \text{ required}$$

$$1 \text{ c.c. TiCl}_3 = 0\text{·}001638 \text{ grm. Fe}$$

100 c.c. of original Rosinduline solution $= 64\text{·}65$ c.c. TiCl$_3$

Corresponding to a copper number of 12·5.

Starches

The application of the " absolute " method (see p. 38) for the estimation of starch in commercial starches depends on the hydrolysis of the starch to glucose, followed by a titration of the osazone. In the following examples no account has been taken of other substances which might be present in the starch (*e.g.* pentosanes) which, when hydrolysed, yield carbohydrates likewise capable of forming osazones and would consequently be included and expressed as starch in the total percentage.

In carrying out the estimation, 1 grm. of the starch is accurately weighed, stirred with distilled water, and heated slowly on a water bath until the starch has gelatinised ; 25 c.c. of hydrochloric acid (sp. gr. 1·16) is then added, the solution made up to about 230 c.c. and heated for an hour in a briskly boiling water bath. The solution is then cooled and made up to 250 c.c. Of this a portion is filtered through a dry filter from any small amount of flocculent precipitate and 10 c.c. of the clear solution is taken for the estimation.

1·075 grms. potato starch was hydrolysed as described and made up to 250 c.c. ; 10 c.c. of the solution required 25·7 c.c. TiCl$_3$ (1 c.c. TiCl$_3 = 0\text{·}002793$ grm. Fe), and as 162 $C_6H_{10}O_5$ $= 336$ Fe, the result corresponds to **80·4** %.

This result, along with those obtained on two other commercial starches, is included in the following table :—

			Starch, %	Moisture, %	Total.
Potato starch	.	.	80·4	17·9	98·3
Rice ,,	.	.	85·4	13·3	98·7
Wheat ,,	.	.	87·1	11·4	98·5

Cellulose

In this case also, substances other than cellulose which might be present but which when hydrolysed are capable of giving carbohydrates which form osazones, have not been considered.

EXAMPLES

1. *Bleached cotton.*—0·6107 grm. of a well-bleached 2/160 cotton yarn was dissolved in the cold in an 80 % solution of sulphuric acid and the solution dilute with 5 times its volume of water. This was heated on the water bath for 20 minutes, cooled and made up to 250 c.c. ; 10 c.c. of the clear solution was converted into the osazone in the manner described under glucose, but with a larger proportion of sodium tartrate. This was reduced with excess titanous chloride and the excess titrated back with Crystal scarlet.

17·1 c.c. $TiCl_3$ was required.

1 c.c. $TiCl_3 = 0·002787$ grm. Fe, and as 162 cellulose = 336 Fe, this gives 94·0 %.

The cotton contained 5·8 % moisture ; total, **99·8** %.

2. *Mercerised cotton.*—0·9028 grm. of the same yarn mercerised under tension and bleached was treated in the same way as the bleached cotton, with the following results :—

25·1 c.c. $TiCl_3$ required.

1 c.c. $TiCl_3 = 0·002742$ grm. Fe, which is equal to 91·9 %.

The product contained 7·9 % moisture ; total, **99·8** %.

472

LITERATURE

ARRANGED IN CHRONOLOGICAL SEQUENCE

WILLIAM GREGOR. Beobachtungen und Versuche über den Menakanite, einem in Cornwall gefundenen magnetischen Sand. *Chem. Ann.* Vol. I. 1791, pp. 40 and 103.

EBELMEN. Sur un nouveau chlorure de titane et sur quelques autres combinaisons de ce metal. *Ann. chim. phys.* 1847, Vol. 20, p. 385.
Ueber eine neue Chlorverbindung des Titans und einige andere Verbindungen dieses Metalles. *J. pr. Chem.* 1847, p. 70. Also *Jahresber.* 1847–8, p. 402.

F. WÖHLER. Ueber die Natur des metallischen Titans. *Ann.* 1850, p. 34.

E. GLATZEL. Ueber die bei der Lösung des Titanmetalls in Säure entetchende Oxidationsstufe und einige neuen Verbindungen des Titans. *Ber.* 1876, p. 1829.

E. KNECHT. Das Titansesquioxid und dessen Salze als Reductions-mittel. *Ber.* 1903, p. 166.
and E. HIBBERT. Das Titantrichlorid in der volumetrischen Analyse. *Ber.* 1903, p. 1549. *Ibid.* 1905, p. 3318 ; 1907, p. 3819 ; 1910, p. 3455.

E. KNECHT. A volumetric process for the estimation of azodyes, nitrocompounds, etc. *J. S. D. & C.* 1903, p. 169.

HOWARD SPENCE. Some compounds of titanium and their application. *J. S. D. & C.* 1904, p. 63.

E. KNECHT and E. HIBBERT. Ueber das symmetrische Trinitroxylenol. *Ber.* 1904, p. 3477.

N. EVANS. Note on the electrolytic preparation of titanous sulphate. *Mem. Manchester Lit. & Phil. Soc.* 1904, Vol. 49, II. p. 1.

A. STÄHLER. Volumetrische Bestimmung des Hydroxylamins mittels dreiwerthigen Titans. *Ber.* 1904, p. 4732.

E. KNECHT. An interesting reaction of copper salts. *Ibid.* 1904, Vol. 48, No. IX. p. 1.
Titanium salts as laboratory reagents. *J. S. D. & C.* 1904, p. 97.
A method for the volumetric estimation of indigo, some basic colours and eosines. *J. S. D. & C.* 1905, p. 292.
The quantitative estimation of some colouring matters in dyed cotton fabrics. *J. S. D. & C.* 1905, p. 3.
On the estimation of Methylene blue. *J. S. D. & C.* 1905, p. 9.
Quantitative estimation of dyestuffs of the triphenylmethane series. *J. S. D. & C.* 1905, p. 111.

F. S. SINNATT. The estimation of picric acid additive compounds. *Proc. Chem. Soc.* 1905, p. 297.

— The estimation of naphthalene by means of titanous chloride. *J. Gas Light.* 1906, p. 288.

E. KNECHT. The analysis of indigo. *J. S. D. & C.* 1906, p. 330.

E. L. RHEAD. Estimation of copper by titanous chloride. *J. C. S.* 1906, p. 1491.

W. P. BLOXAM. The analysis of indigo. *J. S. C. J.* 1906, p. 735.

C. J. BERGTHEIL and R. V. BRIGGS. The determination of indigotine in commercial indigo and in indigo-yielding plants. *J. S. C. J.* 1906, p. 729.

F. S. SINNATT. The determination of nitrates. *Proc. Chem. Soc.* 1906, p. 255.

E. KNECHT. The composition of Aniline blue. *J. S. D. & C.* 1907, p. 119.

— Eine empfindliche Reaction auf Titan. *Chem. Ztg.* 1907, p. 639.

G. GALLO. Determinazione volumetrica del titanio. *Atti accad. Lincei rend.* 1907, p. 325.

F. W. HINRICHSEN. Ueber die maasanalytische Bestimmung von Titan. *Chem. Ztg.* 1907, p. 738.

E. KNECHT. A means of estimating the degree of mercerisation in cotton yarns. *J. S. D. & C.* 1908, p. 68.

— Volumetric process for the estimation of chlorates. *J. S. D. & C.* 1908, p. 201.

S. B. JATAR. Volumetric estimation of iron and chromium by means of titanous chloride. *J. S. C. J.* 1908, p. 673.

H. D. NEWTON. The estimation of iron by permanganate after reduction with titanous sulphate. *Ann. J. Sc.* 1908, p. 343.

B. DIETHELM. Die elektrolytische Reduktion von Titansulfatlösungen. *Inaug. Dissert. Zürich*, 1908.

— and FOERSTER. Elektrolytische Reduktion von Titansulfatlösungen. *Z. f. phys. Chem.* 1908, p. 129.

E KNECHT. The estimation of indigo in dyed cotton fabrics. *J. S. D. & C.* 1909, p. 135.

— Further notes on the estimation of indigo in dyed cotton fabrics. *J. S. D. & C.* 1909, p. 160.

E. HIBBERT. On the volumetric estimation of copper and chromium and of copper, chromium and iron in admixture. *J. S. C. J.* 1909, p. 190.

—— A volumetric method for the estimation of titanium and of titanium and iron in the presence of each other. *J. S. C. J.* 1909, p. 189.

G. E. HOLDEN. The identification of colouring matter in dyed cotton fabrics. *J. S. D. & C.* 1909, p. 47.

A. STÄHLER. Zur Reduktion der Perchlorate durch Titansesquisulfat. *Chem. Ztg.* 1909, p. 759.

V. ROTHMUND and A. BURGSTALLER. Ueber die Bestimmung der Perchlorate durch Reduktion mit Titanosalzen. *Chem. Ztg.* 1909, p. 1245.

V. ROTHMUND. Ueber die Reduktion und Bestimmung der Perchlorate. *Z. f. anorg. Chem.* 1909, p. 108.

E. KNECHT. Reduction of perchlorates by titanous salts. *Proc. Chem. Soc.* 1909, p. 227.

E. KNECHT and HIBBERT. A volumetric method for the estimation of tungsten. *Proc. Chem. Soc.* 1909, p. 227. *The Analyst*, 1911, p. 96.

J. PICCARD. Ueber eine Reaktion auf mehrwerthige Säuren und über eine neue Reaktion auf Titan. *Ber.* 1909, p. 4341.

E. K. FARRER. The assay of perborates. *J. S. D. & C.* 1910, p. 81.

A. GEMMELL. Determination of titanium. *The Analyst*, 1910, p. 198.

E. KNECHT and F. W. ATACK. A new method for the volumetric estimation of molybdenum. *The Analyst*, 1911, p. 98.

L. MOSER. Die Titration von Kupfersalzen mit Titantrichlorid. *Chem. Ztg.* 1912, p. 1126.

P. W. SHIMER and E. R. SHIMER. The volumetric determination of titanium. *Internat. Cong. Appl. Chem. Report*, 1912, p. 445.

F. W. ATACK. A new method for the volumetric estimation of chromium, vanadium and iron in presence of one another. *The Analyst*, 1913, p. 99.

F. ROBINSON. The action of titanous chloride on phenylhydrazine, the substituted phenylhydrazines and p-nitrophenylhydrazones. *J. Manch. Sch. of Techn.* 1913, p. 105. *J. S. D. & C.* 1916, p. 80.

A. EMBLETON. The action of titanous chloride on aldehydes, ketones and their oximes. *Thesis, Manch. Univ.* 1913.

L. RADLBERGER and W. SIEGMUND. Volumetric use of titanous chloride for the determination of invert sugar. *Oest.-Ung. Z. Zucker-Ind.* 1913, p. 34.

H. SALVATERRA. Vergleichende Untersuchungen von Methoden zur Farbstoffbestimmung. *Monatsh.* 1913, p. 1289.

L. MOSER and F. SEELING. Die Bestimmung des wirksamen Sauerstoffes in Persalzen und Waschmitteln mit Titantrichlorid. *Z. f. analyt. Chem.* 1913, p. 73.

F. W. ATACK. The estimation of stannous chloride and of chlorates by means of Methylene blue. *J. S. D. & C.* 1913, p. 9.

B. NEUMANN and R. K. MURPHY. Titanbestimmung durch Titration mit Methylenblau. *Z. f. ang. Chem.* 1913, p. 613.

E. KNECHT. Titanbestimmung durch Titration. *Z. f. ang. Chem.* 1913, p. 734.

J. ZINK and R. LIERE. Bestimmung von Eisen in Wasser mit Titantrichlorid. *J. f. Gasbel.* 1914, p. 956. Also *Wasser und Abwasser*, 1915, p. 113.

C. VAN BRUNT. The volumetric determination of titanium and chromium by means of a modified reductor. *J. A. C. S.* 1914, p. 1426.

T. R. BALL and G. McP. SMITH. The volumetric estimation of titanium by means of ferric chloride. *J. A. C. S.* 1914, p. 1838.

H. SALVATERRA. Ueber die maasanalytische Bestimmung von Nitro- und Nitroso-Körpern mittels Titantrichlorid. *Chem. Ztg.* 1914, p. 90.

E. KNECHT. A new method of valuing hydrosulphites. *J. S. D. & C.* 1915, p. 94.

—— and E. HIBBERT. Estimation of sulphurous acid in sulphites and bisulphites. *J. S. D. & C.* 1915, p. 209.

—— On the quantitative estimation of Alizarin and certain other dyestuffs. *J. S. D. & C.* 1915, p. 241.

E. KNECHT. A rapid method of estimating nitrates. *J. S. C. I.* 1915, p. 126.

A. MONNIER. Emploi du sesquichlorure de titane en analyse qualitative. *Ann. chim. anal.* 1915, p. 1.

L. MOSER. Die maasanalytische Bestimmung der höheren Oxide des Bleis und Mangans mit Titantrichlorid. *Chem. Ztg.* 1915, p. 245.

W. N LEIGH. On the estimation of Alizarin in dyed cotton fabrics and on an attempt to ascertain the composition of Turkey red and other Alizarin lakes. *J. S. D. & C.* 1916, p. 205.

A. MONNIER. Sur l'emploi du sesquichlorure de titane dans les analyses volumétriques par réduction. *Ann. chim. anal.* 1916, p. 109.

F. MACH and P. LEDERLE. Die Verwendung von Titantrichlorid in der analytischen Praxis. *Landw. Vers. Stat.* **90** (1917), p. 191. [A compilation of known methods without acknowledgment.]

O. HACKL. Direkte Bestimmung des gebundenen Eisenoxids in säure-unlöslichen Silicaten. *Chem. Ztg.* 1919, p. 9.

J. G. WILLIAMS. The rapid estimation of perchlorates alone or in presence of chlorates and chlorides. *Chem. News*, 1919, p. 8.

E. KNECHT and L. THOMPSON. An accelerated method of estimating the reducing value of cellulosic substances. *J. S. D. & C.* 1920, p. 255.

W. M. CLARK. Reduction potentials of mixtures of indigotin and indigo white, and mixtures of Methylene blue and methylene white. *J. Washingt. Acad. Sci.* 1920, p. 255.

R. E. CROWTHER and A. D. HEYWOOD. The valuation of sodium hydrosulphite. *J. S. D. & C.* 1920, p. 279.

E. KNECHT and L. THOMPSON. On the volumetric estimation of diazo compounds by reduction. *J. S. D. & C.* 1920, p. 215.

F. L. ENGLISH. The analysis of aromatic nitrocompounds by means of titanous chloride. *J. Ind. Eng. Chem.* 1920, p. 994.

T. CALLAN, J. HENDERSON and N. STRAFFORD. Estimation of the nitro group in aromatic organic compounds. Pt. I. *J. S. C. I.* 1920, p. 86.

W. D. TREADWELL. Reduktion mit Cadmium in der Maasanalyse *Helv. chim. act.* 1921, p. 551 ; 1922, pp. 732 and 806.

W. M. THORNTON and J. CHAPMAN. Notes on the volumetric determination of iron by means of titanous salts. *J. A. C. S.* 1921, p. 91.

T. HENDERSON and A. K. MACBETH. The labile nature of the halogen atom in organic compounds. Pt. I. Titanium reductions of substituted nitroparaffins. *J. C. S.* 1922, p. 892.

A. LAUTERBACH. Die Kontrolle der Hydrosulfitküpen. *Ber. d. 7ten. intern. Verg. d. Chem.-Kol.* 1922, p. 33.

G. BREDIG and J. MICHEL. Zur chemischen Kinetik der Ueber-chlorsäure und ihrer Salze. *Z. f. phys. Chem.* 1922, p. 124.

T. CALLAN and J. HENDERSON. Estimation of the nitro group in aromatic organic compounds. Pt. II. *J. S. C. I.* 1922, p. 157.

W. M. THORNTON. The estimation of copper and iron in presence of each other. *J. A. C. S.* 1922, p. 998.

W. S. HENDRIXSON and L. M. VERBECK. The electrometric standardisation of titanous chloride. *J. A. C. S.* 1922, p. 2382.

J. B. Conant, H. M. Kahn, L. F. Feiser and S. S. Kurtz. An electrometric study of the reversible reduction of organic compounds. *J. A. C. S.* 1922, p. 1382.

W. M. Thornton and H. L. Elderdice. The volumetric estimation of small amounts of phosphorus, using a standard solution of Methylene blue. *J. A. S. C.* 1923, p. 668.

T. Callan and N. Strafford. The analysis of organic rubber vulcanising accelerators. *J. S. C. I.* 1924, p. 1.

G. S. Forbes and L. P. Hall. Measurement of oxidation potentials at mercury electrodes. III. Ter- and bivalent titanium. *J. A. S. C.* 1924, p. 385.

L. Brandt. Ueber die maasanalytische Eisenbestimmung mit Titantrichlorid nach Knecht und Hibbert. *Chem. Ztg.* 1924, pp. 265 and 270.

A. M. Morley and J. K. Wood. The volumetric estimation of titanium. *J. C. S.* 1924, p. 518.

E. Knecht. Titanous salts as reducing agents. *J. C. S.* 1924, p. 1537.

and E. Hibbert. A direct method for the estimation of glucose and other carbohydrates. *J. C. S.* 1924, p. 2009.

- The interaction of methylene blue and glucose in an alkaline medium. Paper read Nov. 21st, 1924, at a meeting of the Society of Dyers and Colourists (Manchester Section).

Abbreviations

Ann. chim. anal. .	Annales de chimie analytique.
Ann. chim. phys. .	Annales de chimie et de physique.
Ann. . . .	Liebig's Annalen der Chemie.
Atti. accad. Lincei rend.. . .	Atti del accademia Lincei rendcondi.
Ber. . . .	Berichte der deutschen chemischen Gesellschaft.
Ber. d. 7ten intern. Verg. d. Chem.-Kol. . .	Bericht der 7ten internationalen Vereinigung der Chemiker-Koloristen. Innsbruck, 1922.
Chem. Ann. . .	Chemische Annalen. Edited by D. L. Crell. Helmstaedt, 1791.
Chem. News . .	Chemical News.
Chem. Ztg. . .	Chemiker Zeitung.
Helv. chim. acta .	Helvetica chimica acta.
Jahresber. . .	Jahresberichte über die Fortschritte der Chemie.
J. C. S. . .	Journal of the Chemical Society (Transactions).
J. A. C. S. . .	Journal of the American Chemical Society.
J. S. C. I. . .	Journal of the Society of Chemical Industry.
J. S. D. & C.. .	Journal of the Society of Dyers and Colourists.
J. pr. Chem. . .	Journal für praktische Chemie.
J. phys. Chem. .	Journal für physikalische Chemie.

J. Ind. Eng. Chem.	Journal of Industrial and Engineering Chemistry.
J. Washington Acad. Sc. . . .	Journal of the Washington Academy of Science.
J. f. Gasbel. . .	Journal für Gasbeleuchtung.
J. Gas Light. .	Journal of Gas Lighting.
Landw. Vers. Stat.	Landwirthschaftliche Versuchs Station.
Mem. Manch. Lit. & Phil. . . .	Memoires of the Manchester Literary and Philosophical Society.
Monatsh. . .	Monatshefte für Chemie.
Oest.-Ung. Z. f. Zucker-Ind. .	Oesterreich-Ungarische Zeitschrift für Zucker-Industrie.
Proc. Camb. Phil. Soc. . . .	Proceedings of the Cambridge Philosophical Society.
Proc. Chem. Soc. .	Proceedings of the Chemical Society.
Z. f. anal. Chem. .	Zeitschrift für analytische Chemie.
Z. f. phys. Chem. .	Zeitschrift für physikalische Chemie.

INDEX TO SUBJECTS

Stannous chloride as a reducing agent, 1
——   , Behaviour towards titanic salts, 6
——   , Estimation of, 79
Starches, Estimation of, 118
Stearic acid, Reduction of oleic acid to, by titanous chloride, 6
Sugars, Estimation of, 36, 115
Sulphide Colours, action of titanous chloride on, 7
Sulphites, Estimation of sulphurous acid in, and bisulphites, 29, 91
Sulphocyanides, Use of, as indicators in estimating iron, etc., 64
Sulphoxalate, Estimation of Sodium formaldehyde, 88
Sulphurous acid, Estimation of, in sulphites and bisulphites, 29, 91

Tannic acid, Behaviour of, towards basic colour, 51
—— ——, Reaction with titanic salts, 3
Tartrate of soda, Use of, in place of Rochelle salt, 7, 65
Tartrazine, Estimation of, 46, 101
Thiocyanate.   See Sulphocyanide.
Thioflavine T, Behaviour of titanous chloride towards, 7
Thio indigo red, Estimation of, 47
Thiosulphate as a reducing agent, 1
Tin, Estimation of, 17, 78
Titanic Potassium Fluoride, 9
—— Potassium Oxalate, 9
Titanic Salts, Estimation of, by iron alum, 10, 70
—— ——, Estimation of, by methylene blue, 10, 70
Titanium, Estimation of, in rutile, 72
——, ——, in ilmenite, 72
——,   , and iron in admixture, 12
Titanous chloride, apparatus for storing and titrating with, 63
—— ——, as a qualitative reducing agent, 1
—— ——, as a quantitative reducing agent, 9
—— ——, Preparation of the solution of, 62
—— ——, properties of, 4
—— ——, standardisation of, 64
—— salts, Interaction of, and ferric salts, 9
        , Properties and qualitative reactions of the, 2
    sulphate, Preparation of, 8
        ——, Reduction of copper sulphate by, 8
—— ——, Use of in estimating nitro compounds, 67
Toluquinone, Estimation of, 41
Tolusafranine, Estimation of, 51
Trinitro cresol, Estimation of, 30
Trinitro toluol, Estimation of, 31
Trinitro xylenol, Estimation of, 31
Triphenyl pararosaniline, Estimation of, hydrochloride, 49
Tungsten, Estimation of, 18, 79
—— ——, and iron, 19
Tungstic acid, Action of titanous chloride on, 6
Turkey red, Estimation of Alizarine in cotton dyed, 111

Vanadic acid, Reduction of, by titanous chloride, 6
Vanadium, Estimation of, 21, 81
——, ——, chromium and iron in admixture, 21

Water, Estimation of dissolved oxygen in, 27

INDEX TO AUTHORS

THE END